case of solutions of phenylfluorenylcarbinols, but the 9-phenylfluorenes are insensitive to light. Racemization is the principal effect of light.[85]

Crude synthetic perylene may be purified by exposing it to a quartz mercury arc.[86] Ether solutions of crude coal-tar show increased ultraviolet transmission after having been similarly irradiated.[87]

On illumination of a cyclohexane solution of carotene, the pressure of oxygen above it in a closed vessel drops initially and reaches a constant value in about three hours. If all or part of the oxygen is then pumped out in the dark, on re-illumination, a pressure rise is observed, indicating an equilibrium between carotene, its oxide and oxygen. But in the case of an octane solution, the oxygen pressure decreases linearly with time without reaching a minimum value.[88]

[85] Lifschitz, I., *Rec. trav. chim.*, **54,** 397 (1935); *Chem. Abs.*, **29,** 5437 (1935).
[86] Postovskii, I. Y., and Bednyagina, N. P., *J. Gen. Chem. (U. S. S. R.)*, **7,** 2929 (1937); *Chem. Abs.*, **32,** 5396 (1938).
[87] Herrick, J. F., and Sheard, C., *Proc. Soc. Exptl. Biol. Med.*, **26,** 33 (1928).
[88] Baur, E., *Helv. Chim. Acta*, **20,** 402 (1937).

Chapter 27

Compounds with Heterocyclic Rings

Oxygen-containing Rings

Essential Oils. The spontaneous transformation of solutions of various odorous substances into a colloidal state by exposure to light has been investigated by Zwaardemaker and Hogewind.[1] In the case of several substances the change occurred only in the presence of ultraviolet light and the resulting colloidal particles were negatively charged. Among the substances studied were eugenol, cresol, guaiacol, carvacrol, citral, cumidine, thymol and hypnone.

A sample of dark yellow distilled lavender oil was found by Quilico[2] to be progressively decolorized by exposure to ultraviolet rays without losing its original fragrance. After one hour, 20 cc. were colorimetrically equivalent to only 19.5 cc. This became 11.5 cc. after 7, 2.5 after 14 and 0.5 cc. color equivalent after 21 hours. Eucalyptus oil was decolorized slightly more rapidly. It was suggested that the formation of oxygenized products caused the slightly lower results in the lavender oil. The essential oil of *Monarda fistulosa* behaves in the opposite manner, becoming brown when exposed to light, according to Badzynski.[3]

Absorption data on a series of oils have been given by Morton[4] and may serve as an aid in the identification of constituents. Maxima are found at 3070 and 2370A (wintergreen), 2810 and 2435A (almond), 2810A (clove), 2770A (thyme), 2860A (cinnamon and cassia), 2850 and 2330A (sassafras), 3110A (lemon), 2380A (mustard), 2320A (cade). Wormseed and mace oils show but little selective absorption. Previous observations on the use of ultraviolet spectrograms in the identification of essential oils were due to Boyer.[5]

It is well known that good quality peppermint oil when used in flavoring certain candies or sugar preparations, such as ordinary mint tablets, loses its fine flavor on long standing. In the laboratory of the senior author, a number of samples of such tablets were exposed to the action of ultraviolet in order to test the stability of certain mint oils in the manufacture of confections. It was found that a few hours' exposure afforded approximately the same aging effect as standing on the shelves for a period of several months. The procedure appears to be a ready method of testing materials of this class to determine quickly their keeping qualities.

It is said that the oxidation of Russian turpentine is more rapid in sunlight

[1] Zwaardemaker, H., and Hogewind, F., *Proc. Akad. K. Wetensch. Amsterdam*, **21,** 131 (1918); *J. Chem. Soc.*, **116,** ii, 14 (1919).
[2] Quilico, A., *Rivista ital. essenze profumi*, **10,** 148 (1928); *Chem. Abs.*, **23,** 2784 (1929).
[3] Badzynski, S., *Wiadomoscki Farm.*, **60,** 689 (1933); *Chem. Abs.*, **28,** 1815 (1934).
[4] Morton, R. A., *Perfumer and Essential Oil Record*, **20,** 258 (1929). See also Harvey, E. H., *J. Am. Pharm. Assoc.*, **19,** 1173 (1930); *Chem. Abs.*, **25,** 5850 (1931); van Os, D., and Dykstra, K., *J. pharm. chim.*, **25,** 437, 485 (1937).
[5] Boyer, J., *Am. Perfumer*, **17,** 389 (1922).
[6] Korotkov, K. N., *Mem. Belloruss. State Acad. Agr.*, **5,** 16 (1927); *Brit. Chem. Abs.*, **B,** 650 (1929); *Lesokhim. Prom.*, **4,** No. 11, 6 (1935); *Chem. Abs.*, **30,** 8658 (1936).
[7] Jorissen, W. P., and Vollgraff, J. A., *Chem. Weekblad*, **12,** 93 (1915); *J. Chem. Soc.*, **108**(ii), 80 (1915).

than in artificial light,[6] due to its ultraviolet rays. Jorissen and Vollgraff [7] claim that the autoxidation of pinene under the influence of the rays from a Uviol lamp increases the electric conductivity of oxygen.

Pinene itself on exposure to ultraviolet rays gives acetylene, ethylene and hydrogen, the liquid containing some isoprene.[8]

Dedichen and Halse [9] expose raw turpentine oil to the action of ultraviolet rays while subjecting it to the action of air or oxygen. The oil is then treated with iron chloride to refine and deodorize it, and obtain a mixture of α- and β-pinenes containing dextrorotatory β-pinenes.

Selenious acid or anhydride may react, under pressure and in the presence of ultraviolet light, with compounds containing the group $CH{=}CHCH_2$, eventually yielding unsaturated α-β-diketones. As starting materials, 1-methane, α-pinene, β-pinene, dipentene-3-methene and eugenol may be employed.[10]

When light acts on mixtures of acetone with some terpene alcohols the formation of pinacols can be confirmed. No other derivatives could be isolated by Scagliarini and Saladini.[11] Terpinol hydrate did not condense with acetone. However, 79.7 gm. of acetone and 53 gm. of geraniol after thirteen months in sunlight gave 63 gm. of acetone, 32 gm. of geraniol and a yellowish residue, boiling at 208-10°C. and composed of $(CH_3)_2C{=}CHCH_2CH_2.C.CH_3{=}CHCH(OH)C(OH)(CH_3)_2$. From a similarly exposed mixture of acetone and menthol about 90 per cent of the original compounds and an analogous condensation product were recovered. Similar results were attained with borneol and acetone.

When air is passed through isoeugenol in which is immersed a lamp emitting ultraviolet rays, vanillin is formed.[12] The rate of oxidation depends upon the penetrating power of the rays. This in turn depends upon the clearness of the isoeugenol and makes necessary the use of the more expensive distilled isoeugenol. Even with this, the oil darkens in a couple of hours and the rate of oxidation rapidly decreases. Another difficulty attending the commercial application of the process is the fact that the rapid circulation of air through the solution as employed in practice caused a considerable loss of isoeugenol by vaporization. In one run in which 30,000 cu. ft. of air were circulated per hour through 800 lbs. of isoeugenol, the loss amounted to about 80 lbs. in eight hours. It was presumed that the oxidation of the isoeugenol was due to the action of ozone formed in the circulated air by the ultraviolet rays. Genthe and Co.[13] claim that the yield of vanillin may reach 95 per cent.

Scagliarini and Saladini [14] exposed 4.7 gm. of fenchone and 4 gm. of toluene in 100 cc. of water in 5-liter flasks full of oxygen to sunlight for nearly a year. Much carbon dioxide was formed and 9.3 gm. of benzoic acid could be separated from eight such flasks in addition to some acetic acid. Similar experiments with fenchone and ethyl alcohol in water gave much carbon dioxide, considerable acetic and some oxalic acids and an undetermined compound with 49.39 per cent carbon and 11.32 per cent of hydrogen. Neither fenchone nor alcohol could be oxidized separately and no easily oxidizable addition product of the two could be detected.

[8] Urbain, E., and Scal, C., *Compt. rend.*, **168**, 887 (1919).
[9] Dedichen, H., and Halse, O. M., U. S. P. 1,253,793, Jan. 15, 1918; *Chem. Abs.*, **12**, 770 (1918).
[10] Schwenk, E., and Borgwardt, E., German P. 608,136, Jan. 17, 1935; French P. 751,807, Sept. 11, 1933; *Chem. Abs.*, **29**, 6246 (1935).
[11] Scagliarini, G., and Saladini, G., *Gazz. chim. ital.*, **53**, 135 (1923); *Chem. Abs.*, **17**, 2281 (1923).
[12] Wood, B. G., *Chem. & Met. Eng.*, **28**, 399 (1923).
[13] Genthe and Co., German P. 224,071.
[14] Scagliarini, G., and Saladini, G., *Gazz. chim. ital.*, **53**, 135 (1923); *Chem. Abs.*, **17**, 2281 (1923).

Similar experiments with pinene and oxalic acid gave carbon dioxide, tar, much unchanged pinene and oxalic acid and some acetic acid.[15]

β-Caryophyllene nitrosite in solution evolves nitrogen when exposed to red light.[16] Its absorption is confined to a narrow band with its head at about 6800A.[17] The quantum yield is, for the nitrogen formed, 0.38 and for the disappearance of the nitrosite as determined optically, 1.37.[18] These values were obtained with oxygen excluded. In its presence, the latter value was higher, 2.9. The gas evolved in the absence of oxygen contained 86.1 per cent nitrogen and 13.9 per cent of nitrogen trioxide.

That nitropiperonal becomes brown on exposure to sunlight was noted by Ekeley and Klemme.[19] Since the isomeric nitropiperonal isolated from a Kahlbaum product is brownish-yellow, it was thought that it might have been produced from the ordinary form by a light reaction. When, however, ordinary nitropiperonal was exposed in thin layers to sunlight and to ultraviolet light, the brown product yielded on recrystallization only nitropiperonal and a tarry brown residue but no isomer.

Piperitone in aqueous acetic acid or alcohol yields (in the light of a quartz mercury arc) needles of a dimer which can be separated into three fractions of the same composition and molecular weight, but which differ in form, melting point and ability to form a semicarbazone. Carvone seems also to form two dimers under these conditions. In sunlight, however, both piperitone and carvone each form only one dimer.[20]

Pimpinellin when subjected in a thin layer to diffused sunlight for two and a half months or to ultraviolet light for 16 hours, and then extracted with ethyl acetate, yields a dimer melting at 237-8°C. When heated four hours on a water-bath with 5-per cent sodium hydroxide this dimer gives furan-2,3-dicarboxylic acid. The action of light upon pimpinellin in cold acetic acid gives a different dimer, melting at 256-7°C., from which the furan derivative could not be isolated after alkaline treatment.[21]

Attempts to isomerize campholic acid by means of ultraviolet light have not been successful [22]; nor does ultraviolet light accelerate the isomeric change of nitrocamphor, or of hydroxymethylene camphor.[23] In the case of aminomethylene-camphor there is a marked acceleration, which ceases when the stimulus is removed. Benzoylcamphor also undergoes isomeric change more rapidly in the presence of radiation, but the acceleration persists after the rays have been withdrawn, possibly because of the liberation of benzoic acid which acts as a powerful catalyst in promoting the isomeric change.

In sunlight, α-naphthylaminocamphor in chloroform forms substituted green compounds with the solvent; the reactions are reversed in darkness. The substance is oxidized in solution in the presence of light, and eventually naphthylamine liberated in the reaction precipitates in the form of hydrochloride.[24] Singh and

[15] For other early observations of this type see Ciamician, G., and Silber, P., *Atti accad. Lincei*, **22**, II, 470; Suida, H., *Monatsh.*, **33**, 1277 (1912); Benrath, A., and v. Meyer, A., *Chem. Abs.*, **7**, 352 (1913).
[16] Kremers, E., *Pharm. Arch.*, **2**, 273 (1899).
[17] Mitchell, S., *J. Chem. Soc.*, 3238 (**1928**).
[18] Hoffman, R. M., *J. Am. Chem. Soc.*, **56**, 1894 (1934).
[19] Ekeley, J. B., and Klemme, M. S., *J. Am. Chem. Soc.*, **50**, 2714 (1928).
[20] Treibs, W., *Ber.*, **63B**, 2738 (1930); *Chem. Abs.*, **25**, 1513 (1931).
[21] Wessely, F., and Dinjasky, K., *Monatsh.*, **64**, 131 (1934); *Chem. Abs.*, **28**, 6435 (1934).
[22] Lipp, P., and Reinartz, F., *Helv. Chim. Acta*, **10**, 611 (1927).
[23] Lowry, T. M., and Courtman, H. R., *J. Chem. Soc.*, **103**, 1214 (1913).
[24] Mitra, B. N., *J. Phys. Chem.*, **35**, 2371 (1931); *Chem. Abs.*, **25**, 5350 (1931).

Bhaduri [25] extended the observations of phototropic change to other solvents. It is absent in methyl, ethyl or ethylene iodides. The oxidation reaction yields α-naphthyliminocamphor and the rotatory power is increased. Both reactions are inhibited by water or sodium ethylate.

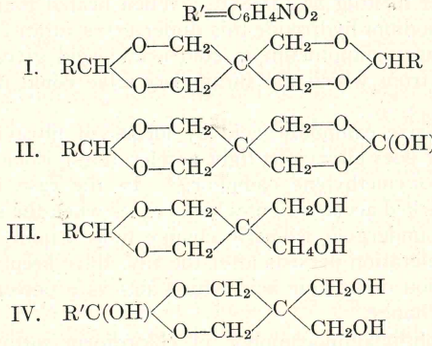
Diazocamphor prepared from inactive camphor, as well as that prepared from the dextro-compound, are decomposed in benzene solution by light of wave-length 2200-3000A, but visible light has almost no action.[26]

The transformation of santonin into photosantonic acid and isophotosantonic acid proceeds by way of intermediate compounds.[27] Photosantonic acid and probably also isophotosantonic acid are very transparent to ultraviolet rays, but santonin is not. No confirmation could be obtained by Piutti of the reported reconversion of yellow santonin into white on boiling. Any visible alteration of santonin crystals under radiation could not be confirmed.

Other Compounds with Oxygen in Rings. 3-Methylcyclohexenone irradiated by a mercury arc for seventeen hours in dilute methanol gives a saturated dimer melting at 144-5°C. and an unsaturated liquid, oily dimer. The photodimer of 3,5-dimethylcyclohexenone melts at 161-2°C. The mother liquor gives an isomer and an unsaturated substance, boiling at 203-5°C. (17 mm.).[28]

Tănăsescu [29] finds that *bis-o*-nitrobenzalpentaerythrito-1-spiran (I) in the solid state becomes slowly colored in sunlight. The change proceeds more rapidly in solution, especially in benzene. (Compare nitrobenzaldehyde.) Only one of the two nitro groups in I reacts with the formation of a compound II. By alkaline saponification of II, *o*-nitrosobenzoic acid and a product III are formed. That III still contains an unaltered nitro- group is shown by its photochemical behavior,

$R' = C_6H_4NO_2$



whereby it is rapidly converted into IV. I rapidly becomes colored on exposure in the solid state to sunshine, the melting point falling in ten days from 166° to 95°C. In ethanol, no crystallizable reaction products can be recovered, but in acetone, ethyl acetate, chloroform, pyridine, and especially benzene, the reaction product is the compound II, of melting point 135°C. In the last-named solvent, the reaction requires only fifteen minutes.

[25] Singh, B. K., and Bhaduri, B., *Trans. Faraday Soc.*, **27**, 478 (1931); *Chem. Abs.*, **25**, 5627 (1931).
[26] Bredig, G., Mangold, P., and Williams, T. G., *Z. angew. Chem.*, **36**, 456 (1923); *Chem. Abs.*, **17**, 3868 (1923).
[27] Piutti, A., *Atti accad. Lincei*, **22**, ii, 92 (1913).
[28] Treibs, W., *J. prakt. Chem.*, **138**, 299 (1933).
[29] Tănăsescu, I., *Bul. soc. stiinte Cluj*, **2**, 111; *Chem. Abs.*, **19**, 2932 (1925). See also Radulescu, D., *Chem. Abs.*, **18**, 1285, 1286 (1924).
[30] Cornubert, R., Andre, M., de Demo, M., Joly, R., Louis, P., Robinet, P., and Strebel, A., *Bull. soc. chim.*, **5**, 513 (1938); *Chem. Abs.*, **32**, 5384 (1938).

Benzylidine derivatives of α-methylcyclohexanone and α-methylcyclopentanone, and of α-isopropylcyclopentanone, undergo oxidation or polymerization on standing. This may be accelerated by ultraviolet light.[30]

4-Methyl-2,6-dianisal-1-cyclohexanone is photosensitive and slowly turns orange-red behind glass. Its pale rose pentabromo-derivative is also photosensitive, turning maroon and violet-red.[31]

Mixtures of indole, various aldehydes and ethyl alcohol, set aside in closed bottles in diffused light for one year and then in sunlight for another year, showed progressive chromatic changes.[32] These were greatest with α-methylindole, less evident with indole and least with scatole. This agrees with the ease of formation of rosindoles from these three compounds. Distilled with steam, the distillate contained unaltered indole, while from the filtered residue the aldehyde was recovered on cooling. In every case there was also recovered from the residue a rosindole. Solutions of diindyl-*m*-methoxy-*p*-hydroxybenzylidene in methanol, ethanol, acetone, chloroform and ethyl acetate are at first colorless, but become intense red on exposure to light and air.

Stobbe and Färber [33] have carried out a series of experiments on the photopolymerization of pure indene. In ultraviolet it resinified.[34]

de Fazi [35] illuminated 2.5 gm. of α-methyl-β-phenylindone in 10 cc. of dry benzene in a quartz test tube with a 1500 c.p. quartz mercury arc for a total of 71 hours during 13 days. Crystals of one form of dimethyldiphenyltruxone separated, white, melting at 307-8°C. From the benzene, unchanged α-methyl-β-phenylindone and the other isomer of the dimethyldiphenyltruxone, yellow, melting at 250-260°, were separated. Each isomer treated with concentrated sulfuric acid gave α-methyl-β-phenylindone. The white isomer is sensitive to light, developing a partially reversible yellow color. In sunlight, the yellow form at the melting point for ten minutes is converted into α-methyl-β-phenylindone. The oxime and phenylhydrazone of α-methyl-β-phenylindone were exposed to ultraviolet light in benzene. A small amount of a new compound, melting at 73-5°C., was obtained, but the oxime and phenylhydrazone of dimethyldiphenyltruxone have not been obtained in this way. From β-phenyl-β′-phenyltruxone irradiated in benzene with ultraviolet for 48 hours a new yellow isomer of β-phenyl-β′-phenyltruxone, melting at 184-5°, was obtained.[36]

The reciprocal reduction and oxidation of ketones and alcohols by light to pinacols and aldehydes occurs also in the case of α,β′-diisoxazole ketone.[37] Ten grams of this compound and 70 cc. of 95-per cent ethanol in a sealed tube exposed to sunlight until the reaction was complete (ten days) yielded 9.7 gm. of α,β′-diisoxazolepinacol, melting 195-6°C. Exposure of the ketone in benzene and in toluene to sunlight led only to traces of reduction products and to unidentified tars. In water, the reaction was very slow, the corresponding acid being formed after six months.

[31] Poggi, R., and Gottlieb, M., *Gazz. chim. ital.*, **64**, 852 (1934); *Chem. Abs.*, **29**, 2152 (1935).
[32] Mingoia, Q., *Gazz. chim. ital.*, **56**, 781 (1926); *Chem. Abs.*, **21**, 1118 (1927).
[33] Stobbe, H., and Färber, E., *Ber.*, **57**, 1843 (1924).
[34] Gunz, A., and Minguin, J., *Compt. rend.*, **152**, 373 (1911); note Weger, M., and Billmann, A., *Ber.*, **36**, 642 (1903); Ciamician, G., and Silber, P., *Ber.*, **46**, 420 (1913).
[35] de Fazi, R., *Gazz. chim. ital.*, **54**, 996 (1924). Dichlorohydrindones from the chlorination of α-methyl-β-phenylindone slowly lose chlorine in diffused light. De Fazi, R., and Pirrone, F., *Gazz. chim. ital.*, **67**, 128 (1937); *Chem. Abs.*, **31**, 6649 (1937).
[36] See also Stobbe, H., and Zschoch, F., *Ber.*, **60B**, 457 (1927).
[37] Freri, M., *Gazz. chim. ital.*, **63**, 419 (1933); *Chem. Abs.*, **27**, 5327 (1933).
[38] Milas, N., and McAlevy, A., *J. Am. Chem. Soc.*, **56**, 1219 (1934).

Ultraviolet light of wave-lengths in the range 4500 to 3600A accelerates considerably the decomposition of furoperacid (obtained from di-furoyl peroxide) either in the solid state or in solution in glacial acetic acid.[38]

Compounds Containing Nitrogen

The lower melting form (65.5-66.5°C.) of methyl-4-benzylidene-3-methylhydantoin-1-acetate when exposed to daylight or ultraviolet light in the presence of a trace of iodine is partly converted into the stereoisomer melting at 98.5-99.5°C. and partly into a polymer melting at 276-278°C.[39]

Some decomposition also occurs with formation of benzaldehyde. The higher-melting stereoisomer similarly yields the lower-melting form and the polymer, the change being preceded by an induction period. 4-Benzylidene-3-methylhydantoin-1-acetic acid also exists in two stereoisomeric forms, melting at 186.5-187.5° and 198.5-199.5°C. The former does not yield measurable quantities of other products when exposed to light for five months. The latter is much more rapidly changed, with production of a small proportion of the lower-melting form and a polymer melting at 293-294°C.

Thymine glycol is easily broken down even in neutral solution by daylight or light from a carbon arc. Lactic aldehyde is formed as an intermediate product which isomerizes into acetol. In weakly alkaline solution, thymine glycol yields urea, acetol and carbon dioxide. In the presence of an oxidizing agent, the products are urea, pyruvic acid and carbon dioxide. With hydrochloric acid solutions or in solutions in which the acidity is produced by the growth of sulfur bacteria, a new anhydride of thymine glycol is produced by carbon arc irradiation. A deep red compound which forms in acid thymine glycol solutions is decolorized upon irradiation to a faint yellow, which shows a green fluorescence in ultraviolet light.[40, 41]

3-Methyl-6,7-benzoylene-β,β-benzopyrrole readily forms solvates and its solutions show different colors which are more or less rapidly decolorized by light, especially ultraviolet light.[42]

α-Picoline in benzene in the presence of anthraquinone gave, after five months of exposure to sunlight, 5.3 per cent of picolinic acid and about 10 per cent of a dark resinous substance soluble in normal sodium carbonate, difficultly soluble in twice normal hydrochloric acid, and giving no precipitate in alcohol with picric acid. Of the anthraquinone, 97.5 per cent was recovered unchanged in experiments of John and Behmel.[43]

Pyridine. Freytag and Neudert find,[44] contrary to Berthelot and Gaudechon, that pyridine is changed by ultraviolet radiations of wave-length less than 3000A. The change is marked by a strong yellow color and an increase in density from 0.97827 to 0.98232 in less than five hours. In methyl alcohol a yellow color begins to appear after four minutes and is marked after two hours. In ethyl alcohol it is first seen in five to ten minutes, in acetone in ten minutes, in amyl alcohol in three minutes and in benzene in thirty minutes. Various salts accelerate the appearance

[39] Hahn, D. A., and Evans, J., *J. Am. Chem. Soc.*, **49**, 2877 (1927).

[40] Johnson, T. B., Baudisch, O., and Hoffmann, A., *J. Am. Chem. Soc.*, **54**, 1106 (1932); Bass, L. J., *Ibid.*, **46**, 190 (1924) has discussed the oxidation of thymine in light. See also Baudisch, O., and Davidson, D., *Ber.*, **58B**, 1680 (1925).

[41] For the photosensitivity of various pyrrole ferrocyanides, see Pratesi, P., *Gazz. chim. ital.*, **65**, 658 (1935).

[42] Scholl, R., Böttger, O., and Stix, E., *Ber.*, **67B**, 1922 (1934).

[43] John, H., and Behmel, G., *Ber.*, **66B**, 426 (1933); *Chem. Abs.*, **27**, 3216 (1933).

[44] Freytag, H., and Neudert, W., *J. prakt. Chem.*, **135**, 15 (1932); *Chem. Abs.* **27**, 724 (1933). Freytag has reviewed his extensive investigations, *Phot. Korr.*, **73**, 17, 37, 57 (1937).

of the color and others inhibit it. Inorganic and organic acids also catalyze the reaction, hydrochloric, nitric, malic and citric acids being particularly effective. Bases are inactive. The zinc chloride compound of pyridine is decomposed into its constituents and the pyridine is changed into the colored photopyridine.

Filter paper impregnated with pyridine, its hydrate or alcoholate, is colored yellow by ultraviolet light. Such papers give various colors on the addition of the salts of aromatic amines. Thus α-naphthylamine hydrochloride gives a light brownish-yellow color and the β-isomer a carmine red color. By the use of such papers, aniline hydrochloride may be detected in dilutions of one part in ten thousand. The test may also be adapted to the detection of pyridine in a dilution of 1:26,840. Since the photopyridine is sensitive to water, the test papers should be protected from moisture. Although the color reactions of irradiated pyridine with primary amines are not in every case sufficiently definite to identify the amine, they may serve to indicate the class to which it belongs.[45] The color and fluorescence of solutions of photopyridine with each of 21 aromatic sulfonic acids were also given. F-acid does not react, probably because of the hindering effect of the sulfonic acid group in position 7. The colors produced in most of these identification tests are changed to yellow or orange by alkalies, but the original color is restored by acids.

"Photopyridine" can be isolated by treating the pyridine solution with zinc chloride. It is obtained as a syrup, ruby-red in color, which decomposes on heating and evolves the odor of pyridine. With boiling β-naphthylamine hydrochloride, it gives red-brown needles, which yield colorless crystals on heating. *p*-Nitroaniline hydrochloride gives an orange color; the ether solution is reddish orange, with a green fluorescence. "Photopyridine" is not formed in the absence of oxygen, but it is not among the products of reaction of pyridine with ozone or hydrogen peroxide. It gives a violet color with a purple-violet fluorescence with sodium, potassium and calcium hydroxides, but not with sodium carbonate, sodium borate, disodium phosphate or ammonia. It gives aldehyde reactions and evolves ammonia on treatment with alkalies, and may be regarded as the ammonium derivative of the enolic form of glutacondialdehyde, $CHO\cdot(CH{=}CH)_2ONH_4$.[46]

"Photopyridine" is formed by wave-lengths in the region 2540 to 2660A.[47] Various derivatives of pyridine are also affected by the lines 2540 and 2650 and to a smaller extent by 2480 and 2400A.[48] With the exception of *sym*-collidine, the photoproducts of the homologous pyridines are similar to photopyridine in structure. These include 2-, 3- and 4-methyl, 2,4- and 2,6-dimethyl, 2,4,6-trimethyl, 2,3,4,5-tetracarboxyl and 2-aminopyridines. The 3-amino- derivative is most affected at the wave-lengths 3650, 3130 and 3020A. The resulting photoproducts of these pyridines may be identified by the colors they give with β-naphthylamine. The derivative from diethyl collidinedicarboxylate is apparently the same as that from its hydrogen derivative. The photoproducts are in most cases destroyed by diffused or direct sunlight. Certain pyridines irradiated by wave-lengths less than 3000A become yellow to yellow-brown in aqueous or alcoholic solutions although the products may not be aldehydic, the enol-aldehyde being converted into the dialdehyde form which is then resinified by free acid.

[45] Freytag, H., *J. prakt. Chem.*, **139**, 44 (1933); *Chem. Abs.*, **28**, 1701 (1934); *J. prakt. Chem.*, **136**, 193 (1933); *Chem. Abs.*, **27**, 2449 (1933).

[46] Feigl, F., and Anger, V., *J. prakt. Chem.*, **139**, 180, 343 (1934); Freytag, H., *Ber.*, **67B**, 1995 (1934); **69B**, 32 (1935).

[47] Freytag, H., and Hlučka, F., *J. prakt. Chem.*, **136**, 288 (1933); *Chem. Abs.*, **27**, 2687 (1933).

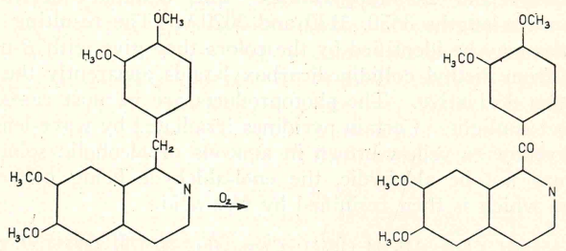
[48] Freytag, H., *J. prakt. Chem.*, **138**, 264 (1933); *Brit. Chem. Abs.* **1933A**, 1304; *Ber.* **69B**, 32 (1936); *Chem. Abs.*, **30**, 2966 (1936) .

A solution of 3-bromo-5-aminopyridine, which assumed an intense color in a short time, gave no aldehyde reactions, but increased in acidity during the first hour and showed the presence of bromide ions. The increasing color possibly acted as an internal filter and slowed the reaction. Oxygen was involved since the coloration began at the surface. The amino- group also may possibly have been attacked. 2-Methyl-5-aminopyridine becomes yellowish-brown but gives no aldehyde reactions and shows no change in pH. Another group of derivatives shows no coloration, but if they contain halogen atoms or esterified carboxyl groups may form halogen ions or free acids on irradiation. Stable toward ultraviolet are 4-chloropicolinic acid and 5-aminopyridine-3-carboxylic acid, which latter has a magnificent blue-violet fluorescence, as well as pyridine-2,3-dicarboxylic acid and coramine, 3-$C_5H_4NCON(C_2H_5)_2$. The chlorine atom is not removed from 4-chloro-2-aminopyridine which becomes colored, possibly because the amino- group is attacked. The rapid brown-yellow coloration of aqueous solutions of 5,6-dichloropyridine-3-aldehyde and the 4,6,2-isomer may be due to attack of the aldehyde group. 4-Iodopyridine-2-carboxylic acid in acid solution liberates hydriodic acid, which is photo-oxidized to iodine and water. Photochemical saponification of diethyl 2,6-dimethylpyridine-3,5-dicarboxylate occurs.

Pure, colorless 2-benzylpyridine, on standing in diffused daylight, becomes yellow-red to brown and shows weak green fluorescence.[49] Filter paper impregnated with a solution of the base (two drops in 10 cc. of alcohol or benzene) turns yellow or brown after one-half to one minute in daylight, gray-brown or greenish after one hour. The product gives a red-purple dye with hot β-naphthylamine solution. With this pyridine derivative, the color of the photoproduct differs somewhat with the wave-lengths used for the irradiation. Longer ones (3650-2700A) give a green discoloration and shorter ones (2650-2480A) a yellow one. The shorter rays produce the usual aldehydic substance and the longer ones, 2-benzoylpyridine with α,β-diphenyl-di-2-pyridylethane.[50]

The reaction has been used in printing fabrics.[51] The fabric is impregnated with a solution of 2-benzylpyridine in 96 per cent alcohol; after evaporation of the alcohol the fabric is covered with a negative plate and exposed to sunlight or ultraviolet rays. When working on cotton, the positive is washed with soap, rinsed and ironed while still moist.

Müller and Dorfman find both pyridine and papaverine, in oxygen-free



Papaverine *Papaveraldine*

[49] Freytag, H., and Müller, A., *Naturwiss.*, **21**, 720 (1933); *Chem. Abs.*, **28**, 710 (1934).
[50] Müller, A., and Dorfman, M., *J. Am. Chem. Soc.*, **56**, 2787 (1934); *Monatsh.*, **65**, 411 (1935).
[51] Freytag, H., and Müller, A., *Monatschr. Textilind.*, **48**, 239 (1933); *Chem. Abs.*, **28**, 5245 (1934).

water vapor, to be unaffected by light,[52] but 2-benzylpyridine, 2-benzoylpyridine and papaveraldine darken. Papaverine in benzene gives 10 per cent of papaveraldine. In the solid state and in presence of oxygen, papaverine and papaveraldine become brown after several hours in mercury light.

Koller [53] states that 6-styryl-2,4-dichloro-3-cyanopyridine (obtained by heating the 6-methyl compound with benzaldehyde) changes in diffused daylight into a substance melting considerably higher and of double the molecular weight of the original compound. That the polymerization consists in the formation of a cyclobutane ring, with destruction of the ethylene bonds of two molecules of the styryl compound, is indicated by the fact that although the original compound is yellow, the polymer is colorless. The polymer does not react with potassium permanganate in cold acetone. Thinking this polymerization might be a property of stilbazoles in general, Koller exposed a number of other compounds of this type to sunlight and to quartz light but was in no case able to effect dimerization. Cantieni [54] finds that, in the presence of 0.001 to 1 per cent of pyridine, there is evolution of carbon monoxide from fructose solutions when exposed to ultraviolet light. The solution also turns brown. More concentrated pyridine solutions did not produce this effect, which is proposed as the basis of a method for the detection of pyridine in very dilute solutions containing not less than 0.001 per cent. Acetone inhibits the formation of the color, which is less readily formed in solutions containing glucose, galactose, sucrose or lactose. Pure pyridine and aqueous solutions more concentrated than 1 per cent are opaque, and solutions more dilute than 0.001 per cent are transparent to ultraviolet light.

Filter paper soaked in an alcoholic solution of quinoline or lepidine, treated with a 0.05 per cent aqueous solution of pyridine and irradiated, slowly becomes yellow. The reaction may be used for the detection of pyridine in the presence of nicotine, since the latter gives only a grayish color.[55]

Phototropy is exhibited by 2,4,4,6-tetraphenyl-1,4-dihydropyridine, as well as by diphenacyldiphenylmethane, 2,4,4,6-tetraphenyl-3,5-dibenzoyl-tetrahydropyran, all three becoming violet in light and reverting to colorless in the dark.[56]

2-Phenyl-3-methyl-quinoline in benzene solution in the presence of anthraquinone gives (on prolonged exposure to sunlight) in addition to dark resinous matter about 3 per cent of 2-phenylquinoline-3-carboxylic acid.[57] 2-Phenyl-6-methylquinoline yielded 8 per cent of the 6-carboxylic acid.[58] 2-*p*-Tolylquinoline gave no acid and and 37.5 per cent was not attacked, but considerable tar was formed. Conquinine [59] sulfate similarly gave 56.0 per cent quininic acid and about 2.6 per cent of a dark resinous substance. Of the base 36 per cent was unaltered, as was 90.9 per cent of the sensitizer.

On long standing in diffuse daylight and more rapidly in sunlight, 6,7-dimethoxy-1-benzyl-N-methyl-1,2,3,4-tetrahydroquinoline-1-carboxylic acid evolves

[52] Henri, V., and Angenot, P., *Compt. rend.*, **201**, 895 (1935), state that light of wavelengths greater than 2750A has no photochemical action on pyridine vapor. Ultraviolet light does not influence the nitration of pyridine in the vapor phase by nitrogen peroxide, Shoruigin, P. P., and Topchiev, A. V., *Ber.*, **69B**, 1874 (1936).
[53] Koller, G., *Ber.*, **60B**, 1920 (1927); *Chem. Abs.*, **22**, 80 (1928).
[54] Cantieni, R., *Helv. Chim. Acta*, **17**, 1492 (1934); **18**, 3, 1420 (1935); *Chem. Abs.*, **29**, 1034 (1935); **30**, 1662 (1936).
[55] Castiglioni, A., *Annali Chim. Appl.*, **27**, 256 (1937); *Brit. Chem. Abs.*, **A** (II), 478 (1937).
[56] de Carvalho, A. P., *Compt. rend.*, **200**, 60 (1935).
[57] John, H., and Behmel, G., *Ber.*, **66B**, 844 (1933); *Chem. Abs.*, **27**, 3713 (1933).
[58] For the behavior of *p*-methoxyquinoline, see Maschmann, E., *Ber.*, **59B**, 2825 (1926).
[59] John, H., and Andraschko, E., *Ber.*, **64B**, 1286 (1931); *Chem. Abs.*, **25**, 4275 (1931).

carbon dioxide and changes to a yellow oil no longer soluble in alkali.[60] Benzylidene quinaldine, exposed to sunlight as a solid or in benzene solution, forms a dimer.[61]

Scholl, Semp and Stix [62] find the arylpyrrolinoanthranolazyls to be nitrogenous, free organic radicals characterized by the absence of all tendency to dimerization, and resembling in stability toward air, acids and alkalies, the common dyes with normal valency. They are unstable toward light, being rapidly decolorized in solution by sunlight.

Histazarin dimethyl ether monoxime is converted by ultraviolet light into a mixture of the *trans* and *cis* forms.[63]

Visible light hastens the oxidation of N-methylphenazonium salts, producing mainly the 4-ketocompound, pyocyanine and phenazine, with small amounts of 2-hydroxyphenazine and 2-keto-N-methylphenazine. Photochemical oxidation of the ethosulfate yields 4-keto-N-ethylphenazine.[64]

Alkaloids

Lesure [65] found considerable ultraviolet absorption by solutions of caffeine, eserine salicylate, apomorphine hydrochloride, and quinine bisulfate. Solutions of eserine salicylate and apomorphine hydrochloride were only slightly discolored and no polarimetric change was observed after an exposure of 15 to 30 minutes. Solutions of cocaine hydrochloride or 1-per cent quinine bichloride or pilocarpine hydrochloride were not effected upon exposure for 30 minutes to the light of a Cooper-Hewitt lamp.

Nicotine. This alkaloid, its zinc chloride double salt, isomethiodide and dimethyliodide in water and in cyclohexane all exhibit a strong absorption band at 2650A.[66]

Ultraviolet light produces a change in nicotine solutions.[67] A 0.1-per cent solution when exposed in a quartz flask at 5 cm. from an ultraviolet source for 15 minutes showed a decided decrease in nicotine content. On the other hand, Custis claimed that a 40-per cent solution of commercial nicotine, when exposed for 30 minutes at 5 cm. from an iron arc showed an increase in the amount of nicotine present. Custis assumed that in this case some nicotine had been synthesized from certain oils present as impurities in the commercial sample. Attempts to synthesize nicotine photochemically have not been successful. Irradiating a 2-per cent aqueous solution of formaldehyde in 6.2*N* ammonia with which was admixed some copper carbonate gave, in experiments by Watson and Vaidya,[68] methylamine but no nicotine. This did not support the view of Bhargava and Dhar that nicotine is formed by the action of light on formaldehyde and ammonia.

The destruction of nicotine has, however, been repeatedly confirmed. In the presence of such sensitizers as potassium chromate, gold chloride, ferric nitrate, iodine and chlorophyll, sunlight causes decomposition of aqueous solutions of the alkaloid, present either as free base, salicylate, tartrate or malonate.[69] In tobacco,

[60] Hahn, G., and Stiehl, K., *Ber.*, **69B,** 2627 (1936); *Chem. Abs.*, **31,** 1815 (1939).
[61] Henze, M., *Ber.*, **70B,** 1273 (1937); *Chem. Abs.*, **31,** 5800 (1937).
[62] Scholl, R., Semp, H., and Stix, E., *Ber.*, **60B,** 1236 (1927); *Chem. Abs.*, **21,** 2684 (1927).
[63] Haq, M., Ray, J. N., and Tuffail-Malkana, M., *J. Chem. Soc.*, 1326 (**1934**).
[64] McIlwain, H., *J. Chem. Soc.*, 1704 (**1937**).
[65] Lesure, A., *J. pharm. Chim.*, **7,** 1,569; *Chem. Abs.*, **5,** 963 (1911).
[66] Lowry, T. M., and Iloyd, W. V., *J. Chem. Soc.*, 1376 (**1929**).
[67] Custis, H. H., *J. Frank. Inst.*, **184,** 878 (1917).
[68] Watson, H. E., and Vaidya, B. K., *J. Indian Chem. Soc.*, **11,** 441 (1934); *Brit. Chem. Abs.*, **A,** 1116 (1934).
[69] Plotnikow, J., and Weber, K., *Chem. Ztg.*, **55,** 237 (1931); *Chem. Abs.*, **25,** 2921 (1931).

the rate of destruction was much less. Orange-red light was believed to be the most effective.

It has been found that, after irradiation from a mercury arc, nicotine solutions have partially lost their effect on the blood pressure of dogs.[70] Wakeham and Tracy [71] found that although the reduction of toxicity might amount to 70 to 75 per cent in 75 minutes, it subsequently returns almost to the original value. Gant [72] observed that after 105 minutes of irradiation, a 0.1-per cent solution of nicotine had lost its basicity and that after 150 minutes it had acquired a slight acidity. At the neutral point the solution had a slight vasopressor activity. The product contained nicotinic acid, methylamine and unchanged nicotine. After 12 hours of irradiation the solution became neutral again, because of the destruction of the nicotinic acid, malonic acid and methylamine. Traces of nitrates, nitrites and ammonia were then found. The irradiation of nicotinic acid gave rise to the same end products. During the irradiation of nicotine, the solution darkened in color. This was ascribed to the formation of yellow oxidation products of nicotinic acid. The color is destroyed by further irradiation.

Quinine. The beautiful fluorescence induced in quinine solutions by visible and ultraviolet light has long been admired. Fabre [73] employed it in measuring the rate of elimination of quinine in the urine.[74] Similar fluorescence methods apply also to hydrastinine and other alkaloids.

The exposure of solutions of quinine salts to ultraviolet rays is said to have no effect on the paralyzing influence of these solutions on *Paramecium* and *Vorticella*,[75] notwithstanding the view of Roskin and Romanova [76] that irradiation increases the toxicity. Giordani [77] holds that, when exposed to ultraviolet rays in the presence of various substances, solutions of quinine undergo transformation into the toxic isomer, quinotoxin. Among the accelerators of the change are urethane and glycerol, which are frequently used in the preparation of solutions for intramuscular or intravenous injection. Alcohol, chloroform and hydrochloric acid were found ineffective in this change.[78] Macht and Teagarden [79] found that fluorescent solutions of quinine and quinidine sulfates became pharmacologically more active after ultraviolet irradiation.

Weigert [80] observed the absorption of oxygen during the irradiation of an aqueous solution of quinine sulfate in contact with air. The reaction velocity increased with increasing concentrations of the quinine sulfate, but was diminished by the addition of an acid. From experiments with gas mixtures containing variable proportions of oxygen, it was found that the reaction velocity increased continuously as the partial pressure of the oxygen diminished. With a mixture of nitrogen and oxygen containing only 0.6 per cent of oxygen, the velocity was about

[70] Higgins, J. A., Ewing, P. L., and McGuigan, H. A., *J. Pharmacol.*, **42,** 213 (1931); *Chem. Abs.*, **25,** 5934 (1931).
[71] Wakeham, C., and Tracy, G. P., *J. Am. Chem. Soc.*, **55,** 1601 (1933); *J. Pharmacol.*, **44,** 295 (1932); *Chem. Abs.*, **26,** 3301 (1932).
[72] Gant, V. A., *J. Pharmacol.*, **49,** 408 (1933); *Brit. Chem. Abs.*, **1934A,** 196.
[73] Fabre, R., *Bull. soc. chim.*, **7,** 1024 (1925).
[74] See also Caujolle, F., *Bull. soc. chim. biol.*, **12,** 299 (1930).
[75] Milanesi, E., *Arch. farm. sperim.*, **46,** 29, 33 (1928); Jirovec, O., and Bouse, V., *Z. Immunitätsf.*, **78,** 100 (1933); *Chem. Abs.*, **27,** 5114 (1933).
[76] Roskin, G., and Romanova, K., *Z. Immunitätsf.*, **62,** 147, 158; **63,** 452 (1929); *Chem. Abs.*, **24,** 5867 (1930).
[77] Giordani, K., *Annali chim. appl.*, **18,** 239 (1928); *Brit. Chem. Abs.*, **1928A,** 907.
[78] For the effect of ultraviolet on monoacyl derivatives of quinic acid, see Josephson, K., *Ber.*, **60B,** 2270 (1927).
[79] Macht, D. I., and Teagarden, E. J., Jr., *J. Pharmacol.*, **22,** 21 (1923).
[80] Weigert, F., *Festschrift W. Nernst*, **1912,** 464; *J. Chem. Soc.*, **102** (ii), 1120 (1912).

thirty times as large as with pure oxygen. The nature of the oxidation process appeared to vary with the proportion of oxygen.

The reaction between quinine and chromic acid has been repeatedly investigated. The early observations of Goldberg[81] seemed to indicate that the velocity is dependent on the extent to which the radiations employed were absorbed by the chromic acid. Luther and Forbes[82] found, however, by using monochromatic radiations, that quinine is the substance which is light-sensitive, the chromic acid acting only as a filter. The total reaction velocity is proportional to the concentration of the hydrogen ion. The reaction appeared to occur in two stages: (1) the formation of "sensitized" quinine with a velocity proportional only to the light absorbed and (2) a reaction between this product and chromic acid with a velocity proportional to the concentration of the latter and of sulfuric acid.

Forbes and co-workers have conducted an elaborate series of investigations on the quantum yield at seven wave-lengths.[83] The quantum yields change with sulfuric acid concentrations at 4050, 3660, 3130 and 2800A and cannot be correlated with the effect of the acid on the extinction of either the quinine or the dichromate. Since the extinction coefficients are additive, it appears improbable that a stable complex is formed, analogous to that of uranyl oxalate. Instead, the reaction occurs in photochemically efficient clusters in the sense in which the term had been employed by Weigert. Irradiation of the dichromic acid did not increase its tendency to react wth non-activated quinine, except possibly at wave-lengths shorter than 2800A. The temperature coefficient of the reaction is 1.12. By graphical methods, the reaction order was found to be zero for quinine and 0.43 for dichromic acid or 0.86 for chromic acid. For sulfuric acid, it is only 0.07, indicating a subordinate role for this reactant. Ten quinine derivatives appear to give similar quantum yields. The values are of the order of 0.065 to 0.027 for quinine and most of the other alkaloids except cinchonine and cinchonidine, for which they are smaller. The low values are not due to the direct photolysis of the alkaloid. Probably a quantum is first absorbed by the quinoline group of the molecule for the logarithm of the quantum yield, at least in the case of quinine, is a linear function of the logarithm of the concentration of excited molecules. The activated molecules then reduce the chromic acid, one activated quinine molecule reacting with one of chromic (not dichromic) acid. In the case of all the alkaloids tested, the secondary hydroxyl group of the activated molecule appeared to be chiefly responsible for the reduction of the chromic acid. The significant suggestion is made that the energy absorbed by the quinoline group may be transferred to the secondary hydroxyl, this transfer occurring only when various photochemically inactive groups are substituted for hydrogen on the opposite side of the quinoline group. The energy transfer may be a resonance phenomenon.[83a] Quinine does not react at 4360A, where absorption is negligible, but decomposes at 4050A where absorption is considerable. With cinchonine, no photolysis occurs at 4050, but does occur at 3660A. With vuzin, the shift is toward the red; absorption is marked at 4360A. The quantum yield decreases as the number of quanta absorbed

[81] Goldberg, E., *Z. wiss. Phot.*, **4**, 95 (1906); *J. Chem. Soc.*, **90** (ii), 514 (1906).

[82] Luther, R., and Forbes, G. S., *J. Am. Chem. Soc.*, **31**, 770 (1909).

[83] Forbes, G. S., Woodhouse, J. C., and Dean, R. S., *J. Am. Chem. Soc.*, **45**, 1891 (1923); Morton, D. S., *J. Phys. Chem.*, **33**, 1135 (1929); Forbes, G. S., Heidt, L. J., and Boissonas, C. G., *J. Am. Chem. Soc.*, **54**, 960 (1932); Forbes, G. S., Heidt, L. J., and Brackett, F. P., Jr., *Ibid.*, **55**, 588 (1933); Forbes, G. S., and Heidt, L. J., *Ibid.*, **55**, 2407 (1933). Forbes, G. S., *Cold Spring Harbor Symposia Quant. Biol.*, **3**, 1 (1935); *Chem. Abs.*, **30**, 6648 (1936). Accurate absorption data for quinine at various acid concentrations were obtained in the course of this work.

[83a] Compare the views of Norrish on the simpler molecules of aldehydes.

in the first centimeter of the reaction mixture increases. The yield is a maximum for quinine at 2800A and for cinchonine at 2540A.

Piperidine metavanadate turns black with liberation of piperidine upon irradiation with ultraviolet light.[84]

Light from a quartz mercury lamp causes a change in the absorption spectrum of ergometrine, which may serve to distinguish it from other ergot alkaloids.[85]

Strychnine in sulfuric acid is unaffected by the addition of small amounts of uranyl acetate; but on exposure to sunlight, the solution becomes violet, as a result of oxidation. This method may be used for the detection of 1×10^{-5} part of strychnine.[86] Under the same conditions of exposure, codeine and morphine give a deep blue color. None of the common alkaloids gives a similar reaction. This blue coloration may also be obtained by using a solution of uranyl acetate which alone has been exposed to the sunlight. This is due to the formation of formaldehyde, the addition of which to a solution of codeine in sulfuric acid with uranium or iron acetates in the absence of sunlight gives an intense blue coloration.

[84] Baudisch, O., and Gates, F. L., *J. Am. Chem. Soc.*, **56**, 373 (1934).

[85] Bennekou, I., and Schou, S. A., *Dansk Tids. Farm*, **10**, 105 (1936); *Chem. Abs.*, **30**, 3944 (1936). See also Harmsma, A., *Pharm. Weekblad*, **65**, 1114 (1928); *Chem. Abs.*, **29**, 235 (1929).

[86] Aloy, J., Valdigué, A., and Aloy, R., *Bull. soc. chim.*, **39**, 792 (1926); *Chem. Abs.*, **20**, 2952 (1926).

Chapter 28

Effects of Light on Halogenation Reactions

Visible light of short wave-length and ultraviolet rays have long been employed to assist in reactions involving halogenation. Chlorination of toluene in light to make benzyl chloride, benzal chloride and benzotrichloride and, by hydrolysis therefrom, benzyl alcohol, benzaldehyde and benzoic acid, is a procedure of long standing. In fact, this application has received considerable commercial use.

During the World War I there was a shortage of amyl alcohol which stimulated extensive investigations on the chlorination of butane, pentane and hexane to monochlor compounds which in turn could be converted into the corresponding alcohols or acetates.[1] Methods based upon these developments have been superseded in practice by entirely different processes, so that these photochemical reactions are at present largely of historical or purely theoretical importance.

It is convenient to discuss halogenation reactions in a separate chapter since they depend for the most part upon the absorption of the light energy by the halogens rather than by the organic reactants. In this discussion, the organic compounds are considered in about the order in which their photochemical reactions have been considered in previous chapters. Due consideration must be given to the possibility that in some instances, particularly those in which unsaturated organic compounds play a part, there may be an absorption of light by the organic substance in addition to that absorbed by the halogen.

Schumacher[2] has reviewed the photochemical reactions of the halogens with aliphatic compounds. Hass, McBee and Weber[3] conducted photochemical chlorinations of propane, *n*- and iso-butane and *n*- and iso-pentane at temperatures of from −60° to 300° and studied the reaction in the dark at temperatures up to 600°C. They separated the products by distillation and identified them rigorously. When pyrolysis temperatures were avoided, no rearrangements of the carbon skeleton occurred during either the photochemical or the thermal chlorinations. Every possible monochloride derivable without such rearrangement was found to be always formed. This generalization extended to all polychlorides studied. Photochlorination of liquid 1-chloro-3-methyl-propane at 7°C. yields 7 or 14 per cent of overchlorinated product when a given amount of chlorine is added slowly or rapidly.[4]

Although Tolloczko[5] obtained by the irradiation of streaming mixtures of chlorine and natural gas at 80 to 100°C. by an ultraviolet lamp, such products as methyl chloride, dichlormethane, carbon tetrachloride and di-, tetra- and hexachlorethane, Baskerville and Riederer[6] found it was the blue rather than the

[1] de Lattre, J., French P. 468,244, Feb. 9, 1914; *J. Soc. Chem. Ind.*, **33**, 953 (1914).
[2] Schumacher, H. J., *Angew. Chem.*, **49**, 613 (1936).
[3] Hass, H. B., McBee, E. T., and Weber, P., *Ind. Eng. Chem.*, **27**, 1190 (1935); **28**, 333 (1936).
[4] Hass, H. B., McBee, E. T., and Hatch, L. F., *Ind. Eng. Chem.*, **29**, 1335 (1937).
[5] Tolloczko, S., *Abhandl. Krakauer Akad. Wissensch.*, **52**, 307; *Chem. Zentr.*, **84**, II, 99 (1913); *Chem. Abs.*, **8**, 1282 (1914).
[6] Baskerville, C., and Riederer, H. S., *Ind. Eng. Chem.*, **5**, 5 (1913).

ultraviolet rays which accelerate the reactions. Brooks, Smith and Essex[7] found similarly that once the chlorination of pentane had been started, it would proceed very smoothly in diffused daylight. Mott and Bedford[8] demonstrated that the flaming carbon arc gave more rapid chlorination of isoamyl chloride, isopentane or benzene than did the quartz mercury arc. Furthermore, little efficiency was lost by the use of glass containers when the flaming arc was used.

In subsequent experiments on the chlorination of methane, Bedford[9] found diffused daylight to produce little or no reaction as long as the percentage of chlorine in the gases was low. Upon suddenly exposing such mixtures to the white flame arc there was an instantaneous explosion of the gases.

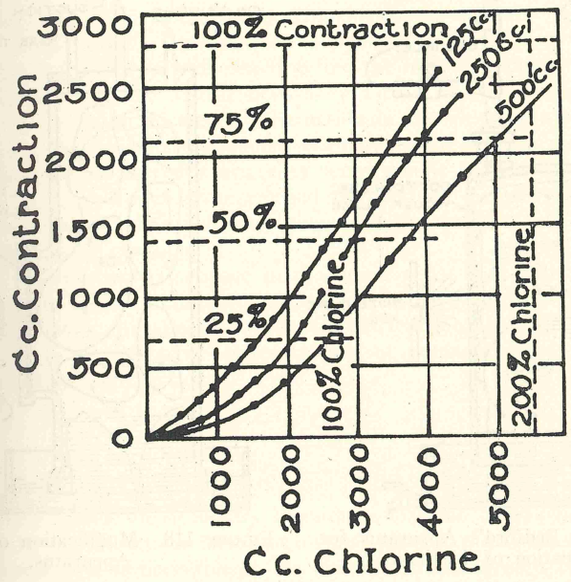


FIGURE 116. Chlorination of Natural Gas.

Figure 116 shows the results reported on the chlorination of natural gas at room temperature in the presence of various quantities of chlorine. After each exposure the gases were cooled by shaking up with water which removed the hydrogen chloride and condensed such reaction products as were liquid at the temperature of the water. The volume of the residual gases was then noted and the contraction from the original gas volume calculated. Starting with three liters of natural gas there was always an unreacting residue of about 200 cc. showing that about 2800 cc. would react with chlorine.*

To avoid the formation of carbon tetrachloride, Bedford tried filling the reaction chamber with cracked ice. He reasoned that in this manner he should obtain only the di- and tri-substitution products, since methyl chloride is a gas at the temperature of ice and the other products might be expected to condense out before forming the tetrachloride. The first experiment, however, indicated the difficulty of securing proper gas circulation. After many variations in the set-up, Bedford employed the apparatus shown

[7] Brooks, B. T., Smith, D. F., and Essex, H., *Ind. Eng. Chem.*, **10**, 511 (1918).
[8] Mott, W. R., and Bedford, C. W., *Ind. Eng. Chem.*, **8**, 1029 (1916).
[9] Bedford, C. W., *Ind. Eng. Chem.*, **8**, 1090 (1916).

* The horizontal dotted lines in Figure 116 represent percentages of the total contraction obtained and aid in the study of the curves.

in Figure 117. An 8-liter, two-necked Woulfe flask, with the bottom removed, was placed over a single ice cake chipped to nearly fill the flask. As the ice melted in the top of the reaction chamber, the flask settled upon it, keeping the ice in the top of the chamber where the cooling is most needed, until the bottom of the flask touched the bottom of the vat. The dotted lines show the point of highest temperature as shown by the melting of the ice. Upon starting the reaction, by means of the white flame arc, with the chlorine content of the gases about one in eight, the circulation was found to be rapid and violent. It was found that 2.6 cubic feet of natural gas gave 166 cc. of reaction products. This is equivalent to about seventeen gallons per thousand cubic feet. This included methylene chloride and chloroform dissolved in the water, which were separated by distillation.

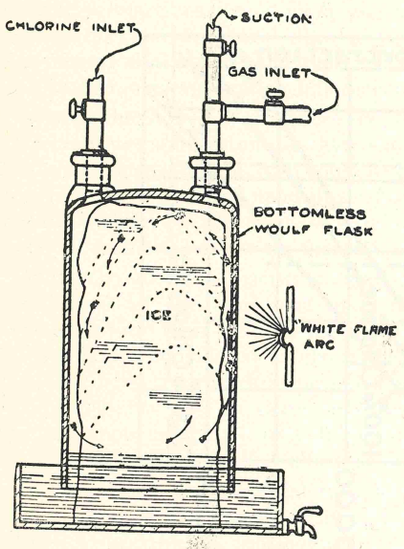


FIGURE 117. Bedford's Apparatus for Chlorination of Methane.

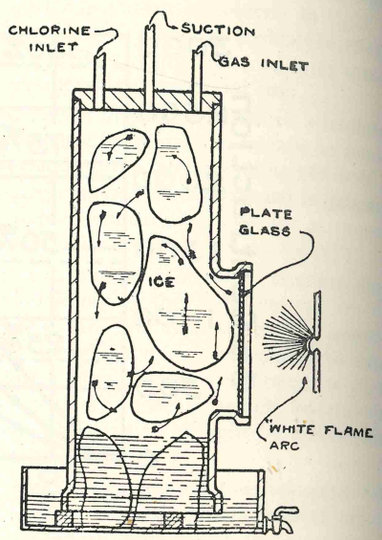


FIGURE 118. Modification of Bedford's Apparatus.

A large wooden reaction chamber, practically duplicating Figure 118, 28" by 28" by 44", inside dimensions, was built for carrying out the reaction on a large scale. In one experiment using 250 cubic ft. of natural gas, the rate of consumption varied from 14 to 30 cubic feet per hour and several gallons of product resulted. The analysis of the liquid reaction product separating out under the water was as follows, the percentages being by volume:

Table 21.—Chlorides from Natural Gas.

Methylene Chloride	Chloroform	Carbon Tetrachloride	Ethane Chlorides
35	35	5	20

The analysis of the part soluble in the water and separated by distillation was:

60	28	1.5	6

About 14 per cent of the reaction product dissolves in the water produced from the melting of the ice by the heat of the reaction. This soluble portion may be entirely recovered by distilling off 5 to 10 per cent of the water, the methyl chloride coming over with the distillate, and the residue being about a 5-per cent solution of hydrochloric acid, provided that no water has been added except that produced by the melting of the ice.

About 135 pounds of ice were necessary for the production of one gallon of product having the composition given above.

According to Padovani and Magaldi,[10] the condition necessary for obtaining a maximum yield of monochloromethane in the photochemical chlorination of methane by use of the mercury arc is to have the ratio of methane to chlorine between 15 to 1 and 19 to 1. Then up to 29 per cent of chlorine goes to methyl chloride and 80 per cent of the total chlorine is utilized. The ratio of methyl chloride to chlorine present in liquid products is 1.75. The efficiency of energy utilization is extremely low. This is the most serious obstacle to the commercial utilization of the process.

Comparatively few theoretical studies have been made of these chlorination reactions. In the case of methane, the chlorination is a chain process, quantum yields of 10^4 being found.[11] The reaction is strongly inhibited by traces of oxygen.

From an analogy between this reaction and the hydrogen-chlorine combination, Jones and Bates[12] suggest that it occurs by virtue of chlorine atoms and free methyl radicals, the latter formed by the action of the chlorine atom on methane. From their rate experiments, conducted with a flowing system in a glass spiral illuminated by a Pyrex mercury arc, they were unable to determine whether the methyl group or a hydrogen atom carried the chains. Simple considerations of the collision mechanism of a chlorine atom with the methane molecule made the former seem the more probable.

The total chlorination of pentane in the liquid phase and with rigid exclusion of oxygen which is an inhibitor was studied by Stewart and Weidenbaum.[13] Using light of 3650A, they found a quantum efficiency of 192. The reaction rate is proportional to the chlorine concentration at constant light intensity. The mechanism involves the reactions:

$$Cl_2 + h\nu \longrightarrow Cl + Cl.$$
$$Cl + C_5H_{12} \longrightarrow HCl + C_5H_{11}$$
$$C_5H_{11} + Cl_2 \longrightarrow C_5H_{11}Cl + Cl.$$

This mechanism fulfills the necessary conditions that the overall reaction, as well as every step, be exothermic or have but a small energy of activation. The correct experimental rate law is derivable if the chain-terminating step is taken to be a formation of chlorine molecules at the wall or inert molecules.

Benrath and Hertel[14] found that perfectly purified and dried carbon tetrachloride contains free chlorine after several days of exposure to light. The amount of decomposition is not sufficiently great to hinder the use of carbon tetrachloride as a solvent in which to study the photochlorination of various aliphatic compounds. Since halogen compounds are frequently used as solvents, it may be noted that chloroform is comparatively unstable under the influence of ultraviolet radiation[15] and further that trichloroethylene is on occasions a somewhat fickle solvent disengaging hydrogen chloride.[16]

During the period from 1912 to about 1925 a considerable number of patents dealing with the chlorination of various saturated hydrocarbons were issued. It

[10] Padovani, C., and Magaldi, F., *Giorn. Chim. Ind. Applicata*, **15**, 1 (1933); *Chem. Abs.*, **27**, 3443 (1933).
[11] Coehn, A., and Cordes, H., *Z. physik. Chem.*, **9B**, 1 (1930).
[12] Jones, L. T., and Bates, J. R., *J. Am. Chem. Soc.*, **56**, 2282 (1934).
[13] Stewart, T. D., and Weidenbaum, B., *J. Am. Chem. Soc.*, **57**, 1702 (1935).
[14] Benrath, A., and Hertel, E., *Z. wiss. Phot.*, **23**, 30 (1924).
[15] Kailan, A., *Monatsh.*, **38**, 537 (1917); *J. Chem. Soc.*, **112**, i, 209 (1917).
[16] Elsner, W., *Chem. Z.*, **41**, 901 (1917).

is feasible here to do no more than cite these, since most deal with details of apparatus for applying ultraviolet rays.[17]

Graul and Hanschke[18] boiled normal hexane in an enameled vessel on a water-bath, and passed the vapors through a vertical fractionating column into a second vessel in which they were mixed with chlorine. The mixture, containing an excess of hexane vapor, passed into a third vessel in the middle of which a mercury lamp was burning. The vapors leaving this reaction vessel were passed through a condenser in which the chlorhexane and the excess of hexane condensed and passed through a siphon into a

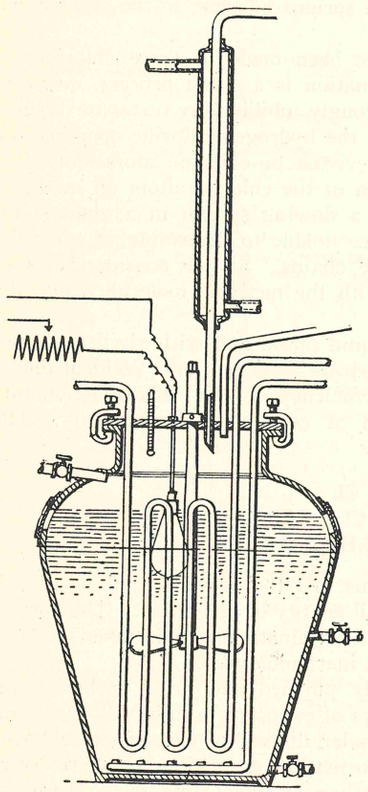


FIGURE 119.

Apparatus of Brooks, Essex and Smith for Chlorinating Liquid Hydrocarbons.

distillation vessel, while the hydrochloric acid formed during the process was allowed to escape from the circuit. The fractionating column attached to the first vessel was maintained at a temperature that allowed only hexane to pass, while chlorhexane remained in the still and increased in quantity. To prepare monochlor-isoheptane, a Galician petro-

[17] Blanc, C., U. S. P. 1,248,065, Nov. 27, 1917; Rodebush, W. H., U. S. P. 1,402,318, Jan. 3, 1922; Okinaka, T., and Sakai, S., Japanese P. 35,994; *Chem. Abs.*, **15,** 1535 (1921); Japanese P. 39,940, July 16, 1921; *Chem. Abs.*, **16,** 3560 (1922); DuPont Co., French P. 453,406, June 21, 1913; Pfeiffer, I., and Szarvasy, E., U. S. P. 1,012,149, Dec. 19, 1911; *J. Soc. Chem. Ind.*, **32,** 91 (1912); Snelling, W. O., U. S. P. 1,523,563, Jan. 20, 1925; 1,285,823 and 1,325,214; *Chem. Abs.*, **14,** 369 (1920); U. S. P. 1,271,790, July 9, 1918; 1,523,563, Jan. 20, 1925; Keyes, F. G., U. S. P. 1,237,652, Aug. 21, 1917; Sparre, F., and Masland, W. E., U. S. P. 1,379,367, May 24, 1921; Tompkins, H. K., British P. 780, Jan. 18, 1915; *J. Soc. Chem. Ind.*, **34,** 1225 (1915); Leiser, R., and Ziffer, F., U. S. P. 1,459,777, June 26, 1923; Söll, J., and Runkel, K., German P. 491,316, Dec. 12, 1922; Keyes, F. G., U. S. P. 1,198,356, *Chem. Abs.*, **10,** 2315 (1916); Lacey, B. S., U. S. P. 1,308,760; *Chem. Abs.*, **13,** 2219 (1919).

[18] Graul, O., and Hanschke, G., U. S. P. 1,032,822, July 16, 1912.

leum fraction consisting chiefly of isoheptane was placed in a lead-lined vessel provided with fractionating column and raised to the boiling point, at a pressure of 50 mm. of mercury. The vapors were mixed with chlorine and passed through a vessel containing a mercury lamp. In order to chlorinate 10 parts of hydrocarbon, about 7 parts of chlorine were necessary. The chlorination product consisted chiefly of a mono-chlor-isoheptane which boils at about 140°C. and contains 26.5 per cent of chlorine. By treating, in a similar manner, the repeatedly purified fraction of Galician petroleum which boils at from 75° to 81°C., a product was obtained boiling between 135° and 145°C., and containing 29.1 per cent of chlorine, whereas pure monochlorhexamethylene contains theoretically 29.8 per cent of chlorine.

A few patents dealt with the chlorination of liquid hydrocarbons. Brooks, Essex and Smith[19] emphasized the necessity of introducing the chlorine in minute bubbles at a point in the liquid remote from that at which the rays of light enter, and agitating so as to maintain a large excess of hydrocarbon in the zone where the reactions occur. It was believed that this led to the production chiefly of monochlor- products (butyl, pentyl and hexyl chlorides) from gasoline, useful in the manufacture of artificial "amyl acetate." (See Fig. 119.) The unchanged oil is separated from the chlorides by fractional distillation. If dichlorides are to be produced, the container is charged with mono-chlorides rather than with hydrocarbons. Even solid materials as paraffins may be used if they are melted or dissolved in carbon tetrachloride.

Brooks and Padgett[20] chlorinated solar oil in this manner and subjected the dichloride obtained to a high temperature in the presence of a catalyst. This treatment split off hydrochloric acid and produced unsaturated hydrocarbons with an iodine number of from 120 to 150 suitable for the formation of "drying" films like those of linseed oil.[21]

After a lapse of nearly ten years, patents in this field have again begun to appear. In a continuous flow method for the vapor phase photochlorination of the saturated aliphatic hydrocarbons with three to five carbon atoms, as butane or isobutane, Britton, Coleman and Hadler[22] employ surfaces in contact with the reacting mixture cooled to a temperature (below 250°) which prevents the formation of chloroölefines. For preparing monochloro- derivatives, Teichmann, Klein and Rathemacher[23] treat a paraffin hydrocarbon material, such as a pentane fraction, in the liquid phase while exposed to ultraviolet light with a reagent consisting of polychloro- derivatives of the hydrocarbons. The reaction products are then submitted to a reaction with chlorine under such pressure as to maintain the reaction products in the liquid phase, so that monochloro- and polychloro- compounds and hydrogen chloride are formed. The hydrogen chloride is removed and the chloro-compounds separated into two fractions, one containing the mono- and the other the polychloro- derivatives.

According to Sharp,[24] a material containing a high percentage of propane and a compound such as the lower chloropropanes convertible into a trichloropropane are treated with chlorine in the presence of a chlorination catalyst such as copper chloride or ferric chloride under the influence of actinic rays, and in a plurality of stages at increasing temperatures.

In their studies of the higher polychlorides obtainable by the chlorination of 2-chloro-2-methylpropane in the liquid phase, Rogers and Nelson[25] used ordinary incandescent lamps for activation. They were chiefly concerned with the characterization of the various higher chlorides obtainable by fractional distil-

[19] Brooks, B. T., Essex, H., and Smith, D. F., U. S. P. 1,191,916, July 18, 1916.

[20] Brooks, B. T., and Padgett, F. W., U. S. P. 1,220,821, March 27, 1917.

[21] Details of another chlorination process involving both liquid and vapor phase chlorination successively have been given by Boyd, H. T., U. S. P. 1,293,012, Feb. 4, 1919.

[22] Britton, E. C., Coleman, C. H., and Hadler, B. C., U. S. P. 1,954,438, April 10, 1934, to Dow Chemical Co.; *Chem. Abs.*, **28,** 3739 (1934).

[23] Teichmann, C. F., Klein, H., and Rathemacher, C. P., U. S. P. 2,015,044, Sept. 17, 1935; *Chem. Abs.*, **29,** 7338 (1935).

[24] Sharp, W. E., U. S. P. 2,001,039, Aug. 6, 1935; *Chem. Abs.*, **29,** 6252 (1935).

[25] Rogers, A. O., and Nelson, R. E., *J. Am. Chem. Soc.*, **58,** 1027 (1936).

lation. There were obtained from 3500 cc., 305 cc. of $(CH_3)_2CClCH_2Cl$, 600 cc. of $(CH_3)_2CClCHCl_2$, 875 cc. of $(CH_3)_2CCl(CH_2Cl)_2$, 460 cc. of 1,1,2,3-tetrachloro-2-methylpropane and 130 cc. of $ClC(CH_2Cl)_3$. Chlorination of 400 cc. of the first fraction of these gave 140 gm. of $(CH_3)_2CClCCl_3$. Chlorination of the $CH_3CH(CH_2Cl)_2$ gave the 1,2,3,-trichloro- and 1,1,2,3-tetrachloro- derivatives. $(CH_3)_2CClCH_2Cl$ gave the 1,1,2- and the 1,2,3-trichloro- derivatives. In general, the presence of a chlorine atom on a carbon atom promoted further substitution on that atom.[26]

Chlorination of Chloroform. Gault and Truffault[27] found chlorine without action on chloroform in the dark or when exposed to radiations of wave-length longer than about 6390A. Violet light had a slight effect and ultraviolet rays (3000 to 3400A) a great one. The reaction begins at −5°C. and becomes rapid at 5-10°C. Dry chlorides of calcium, zinc or aluminum act to some degree as catalysts, but ferric chloride appeared to inhibit the reaction entirely by acting as an internal filter. Even in the absence of any stimulus other than ultraviolet, the reaction is complete and carbon tetrachloride results. Benrath and Hertel[28] observed an induction period of about thirty minutes when the reaction was carried out in carbon tetrachloride.

In the vapor state, the rate of the reaction at 50 to 70°C. is proportional to the square root of the chlorine concentration and to the square root of the absorbed energy.[29] The temperature coefficient is 1.45 between 50 and 60°C. Oxygen practically suppresses the formation of carbon tetrachloride and yields phosgene. The reaction has a chain mechanism, with the following four reactions:

$$Cl_2 + h\nu \longrightarrow Cl + Cl.$$
$$Cl + CHCl_3 \longrightarrow CCl_3 + HCl$$
$$CCl_3 + Cl_2 \longrightarrow CCl_4 + Cl$$
$$CCl_3 + CCl_3 \longrightarrow Cl_2 + 2CCl_4.$$

Chapman[30] finds the average quantum yield of hydrogen chloride 1.70 in the chlorine-sensitized photoöxidation of chloroform in carbon tetrachloride solution; in the vapor phase it is about 100.

In the replacement of bromine by chlorine in bromotrichloromethane, Noddack[31] reported a quantum yield of unity at high concentrations. This was decreased to about 0.2 when dilute solutions were used. A later study by Grüss[32] indicated a value of 0.88, independent of the concentration. These workers assumed that the reaction is a simple replacement, and determined the rate of the change by measuring the absorption changes which attended the liberation of the bromine. The possibility that an error might arise because of the formation of a bromochloride led Vesper and Rollefson[33] to examine the reaction again. They found the reaction more complicated than had been assumed, a chain process being involved. They employed the group of lines at 3660A isolated from the mercury

[26] For the chlorination of methyl chloride and dichloromethane, see Dachlauer, K., and Schmitzler, E., French P. 816,990, Aug. 21, 1937, to I. G. Farbenind. A.-G.; *Chem. Abs.*, **32**, 2142 (1938); German P. 657,978, May 25, 1938; *Chem. Abs.*, **32**, 5856 (1938).

[27] Gault, H., and Truffault, R., *Compt. rend.*, **179**, 467 (1924); *Chem. Abs.*, **19**, 35 (1925).

[28] Benrath, A., and Hertel, E., *Z. wiss. Phot.*, **23**, 30 (1924).

[29] Schumacher, H. J., and Wolff, K., *Z. physik. Chem.*, **25**, 161 (1934). See, however, Schwab, G. M., and Heyde, V., *Z. physik. Chem.*, **B8**, 147 (1930).

[30] Chapman, A. T., *J. Am. Chem. Soc.*, **56**, 818 (1934).

[31] Noddack, W., *Z. Elektrochem.*, **27**, 359 (1921).

[32] Grüss, H., *Z. Elektrochem.*, **29**, 144 (1923).

[33] Vesper, H. G., and Rollefson, G. K., *J. Am. Chem. Soc.*, **56**, 1455 (1934).

arc radiations by means of a filter, in order to avoid the decomposition of bromotrichloromethane which Paterno[34] had found to occur in the region below 3350A. By spectrographic methods and a knowledge of the original chlorine concentration, it was possible to calculate the concentrations of chlorine, bromine and bromine chloride present at any time. The reaction was found to be

$$Cl_2 + CBrCl_3 \longrightarrow BrCl + CCl_4$$

no hexachloroethane being formed. (A second reaction in which free bromine and two molecules of carbon tetrachloride are formed occurred to only a negligible extent.) The rate of the reaction varied directly with the chlorine concentration raised to a power between 1. and 1.5, and with the bromotrichloromethane concentration to a power somewhat greater than 0.5. The rate was markedly retarded by bromine chloride. It was not affected by the total pressure, but was doubled by increasing the temperature from 28 to 50°C. No dark reaction occurred. The incident light intensity enters the rate law by a power slightly greater than 0.5. Inert gases had practically no effect on the reaction rate. The quantum yield was found to be much higher than previous workers had indicated. It reached at least thirty at the beginning of the reaction but decreased to less than ten when the concentration of the bromine chloride had become large. The quantum yield could be decreased by lowering the concentrations of either of the two reactants.

A little attention has been devoted to iodination reactions of the saturated simple paraffins. Iodine derivatives of the paraffin series, excepting liquid methane, may be obtained by mixing the hydrocarbon in the dark with hydriodic acid and subjecting the mixture to the action of light rays of short wave-length or to the silent electric discharge. The reaction temperature may be reduced, according to the Badische Co.[35] by operating under diminished pressure.

The photochemical formation of phosgene in the action of chlorine on chloroform in the presence of oxygen is inhibited by such substances as methanol, ethanol and ammonia. The duration of the inhibition is proportional to the quantity of the inhibitor.[36] It is due to the removal of the chlorine atoms by the inhibitor, since, if the latter is first chlorinated, it ceases to affect the reaction.

Unsaturated Hydrocarbons

A few early patents were devoted to the chlorination of unsaturated hydrocarbons. Eldred and Mersereau[37] state that olefins produced by cracking oil may be treated with chlorine in the presence of rays of a mercury-vapor lamp in order to obtain chlorinated products. They noted that the operation requires caution since the reaction is violent. Ragaz, Paillard and Briner[38] passed 30 cc. of kerosene over iron turnings in an iron tube at temperatures of 550 to 800°C. and obtained about 13 liters of gas containing about 30 per cent of unsaturated compounds. By passing a slight excess of chlorine into the gas as it was formed in diffused daylight about 57 per cent of the gas was converted into a mixture of chlorinated hydrocarbons. This gave fractions distilling at 65-100°C., 70.69 per cent chlorine; 100-125°C., 73.41 per cent; 125-150°C., 75.14 per cent. These were mobile fluids whose flash points were 5°C., 19°C. and 36°C., respectively.

[34] Paterno, E., *Jahresb. Chem.*, **24**, 259 (1871).

[35] Badische Anilin u-Soda Fabrik, German P. 266,119, Oct. 31, 1911.

[36] Schumacher, H. J., and Sundhoff, D., *Z. Elektrochem*, **21**, 499 (1935).

[37] Eldred, B. E., and Mersereau, G., U. S. P. 1,234,886, July 21, 1917.

[38] Ragaz, Y., Paillard, H., and Briner, E., *Helv. Chim. Acta*, **8**, 225 (1925); *J. Soc. Chem. Ind.*, **1925B**, 580.

They readily dissolved sulfur, iodine or white wax. The use of ultraviolet light or the addition of catalysts did not improve the yield of non-flammable solvents.

In a patent of the I. G. Farbenindustrie [39] 1,1,2-trichloroethane is obtained by direct addition of vinyl chloride and chlorine gases without the use of a solvent by the aid of light or heat.

The rate of addition of chlorine to ethylene is accelerated by the rays of the mercury arc.[40] Trichlorohydrin is obtained by further chlorination, in the presence of a sulfur compound such as sulfur dioxide, sulfur chloride, sulfuryl chloride, of propylene chloride or a similar compound obtained by saturating unsaturated hydrocarbons with chlorine.[41] The sulfur compound should not exceed 1 per cent of the amount of chlorine. Sulfur dioxide and chlorine may either be introduced separately or mixed. The reaction is effected in direct sunlight or ultraviolet rays or the light of the flaming arc. The product is separated from any unchanged propylene chloride by distillation.

In the chlorination of propylene dichloride with metallic iron present, ultraviolet light and low temperatures favor the production of $CHCl(CH_2Cl)_2$. Higher temperatures without irradiation favor the formation of $CHCH_3Cl.CHCl_2$.[42]

Stewart and Weidenbaum [43] investigated the reaction between chlorine and ethylene, using light from a 500-watt tungsten lamp and filters. At 4360A the quantum yield appeared to be large. During the early part of the reaction there appeared to be a logarithmic relation between the chlorine pressure and the time, as well as a linear relation between the reaction rate and the light intensity. The experimental results could be expressed by mechanisms involving either atomic chlorine or Cl_3; the collision efficiency of ethylene with either should be high, since the reaction rate is independent of the ethylene concentration over wide limits. The rate was thought to be determined by the rate of liberation of atomic chlorine from an intermediate, $C_2H_4Cl_3$. Any hydrogen added to the reaction vessel appeared not to react until the ethylene-chlorine reaction had gone to completion. When the reaction was carried out in solution in ethylene dichloride, it was very rapid and less than 10 per cent of the chlorine was involved in substitution reactions. But with pentane as the solvent, from 37 to 73 per cent of the chlorine entered into substitution and this could be increased by increasing the ethylene-to-chlorine ratio.

Dickinson and Leermakers [44] found it possible to chlorinate tetrachloroethylene in carbon tetrachloride solution by the action of blue light in the absence of oxygen. The chlorination proceeds as a chain reaction with a large quantum yield (300-2500) and at a rate proportional to the square root of the intensity of illumination. In the presence of oxygen, in place of a simple inhibition, there occurs a chlorine-sensitized oxidation to trichloroacetyl chloride and phosgene.[45] This reaction proceeds in solution with a comparatively small quantum yield (1 to 2.5) and at a rate proportional to the light intensity, and to the chlorine concentration.[46] The work on the chlorination of tetrachloroethylene has been extended

[39] British P. 298,084, Sept. 30, 1927, to I. G. Farbenind. A.-G.; *Brit. Chem. Abs.*, **B,** 122 (1929).
[40] Kinumaki, S., *J. Chem. Soc. Japan,* **54,** 142 (1933); *Chem. Abs.,* **27,** 2369 (1933).
[41] British P. 168,676, Feb. 18, 1921, to Glysyn Corporation; *Chem. Abs.,* **17,** 771 (1923).
[42] Levine, A. A., and Cass, O. W., British P. 471,188, Feb. 28, 1936, to E. I. DuPont de Nemours and Co.; *Brit. Chem. Abs.,* **B,** 1309 (1937).
[43] Stewart, T. D., and Weidenbaum, B., *J. Am. Chem. Soc.,* **57,** 2036 (1935).
[44] Dickinson, R. G., and Leermakers, J. A., *J. Am. Chem. Soc.,* **54,** 3852 (1932).
[45] Cf. Besson, A., *Compt. rend.,* **121,** 125 (1895).
[46] See also Dickinson, R. G., and Leermakers, J. A., *J. Am. Chem. Soc.,* **54,** 4648 (1932).

to the gas phase by Dickinson and Carrico,[47] who conducted it at temperatures below 40°C. and followed the rate by measuring in an ingenious apparatus the change in pressure. In the absence of oxygen, the chlorination proceeded with the formation on the walls of the vessel of colorless crystals having the odor of hexachloroethane. In the presence of oxygen little if any chlorination occurred, but phosgene and trichloroacetyl chloride were obtained. The rate of the chlorination was proportional to the chlorine concentration and to the square root of the intensity of the light absorbed.

In the chlorine-sensitized photo-oxidation in the gas phase about 300 molecules of tetrachloroethylene were oxidized for each quantum (3358A) absorbed. There was no strong dependence of the yield on the concentrations or light intensity.

The chlorination of *trans*-dichloroethylene at 80-95°C. by the 4358A line of the mercury arc is a chain reaction.[48] For a chlorine pressure of 100 mm. and an absorption of 10^{16} quanta per minute, the quantum yield is 7×10^3 and the temperature coefficient 1.13. For pressures of the dichloride greater than 20 mm., the rate is given by

$$\frac{d(C_2H_2Cl_4)}{dt}=k(I_{abs})^{\frac{1}{2}}(Cl_2)$$

The mechanism involves the reactions:

$$Cl + C_2H_2Cl_2 \longrightarrow C_2H_2Cl_3$$
$$C_2H_2Cl_3 + Cl_2 \longrightarrow C_2H_2Cl_4 + Cl$$
$$2C_2H_2Cl_3 \longrightarrow 2C_2H_2Cl_2 + Cl_2$$

The reaction is strongly inhibited by the presence of oxygen.

The reaction with the *cis*- compound is very similar.[49] In this case, a sensitized oxidation with greater quantum yield does not occur. In the chlorination of trichloroethylene, the rate of formation of pentachlorethane is proportional to the chlorine concentration and the square root of the energy absorbed. Only at pressures below 5 mm. is it dependent on the concentration of trichloroethylene. The temperature coefficient is 1.20. The quantum yield (chlorine at 100 mm. and 1.7×10^{14} quanta per second) is 700. The reaction is inhibited by oxygen and a sensitized oxidation occurs.

Notwithstanding the many instances of inhibition of chlorination processes by oxygen, Willard and Daniels [50] find the rate of photobromination of liquid tetrachloroethylene with light of 4360A to be increased by small amounts of oxygen. But when one atmosphere of oxygen is used, the photobromination is almost completely inhibited, probably because of a bromine-sensitized oxidation. The bromination products inhibit the reaction but the concentration of tetrachloroethylene is not important. The quantum yield varies enormously from 24 to only 0.009 (moles of bromine disappearing per quantum) with values of 1 to 5 the most frequent. The free radical C_2Cl_4Br is believed to play a part in the reaction mechanism and it is suggested that the life period of this radical is much shorter at higher temperatures and that it is stabilized by oxygen.

These authors also found that the photobromination of chloroform does not occur at 2650A in the absence of oxygen, although a reaction takes place in the

[47] Dickinson, R. G., and Carrico, J. L., *J. Am. Chem. Soc.,* **56,** 1473 (1934); see also Stewart, T. D., and Smith, D. M., *Ibid.,* **51,** 3082 (1929).
[48] Müller, K. L., and Schumacher, H. J., *Z. physik. Chem.,* **B35,** 285 (1937).
[49] Müller, K. L., and Schumacher, H. J., *Z. physik, Chem.,* **B35,** 455 (1937); *Z. Elektrochem,* **43,** 807 (1937).
[50] Willard, J., and Daniels, F., *J. Am. Chem. Soc.,* **57,** 2240 (1935).

presence of small amounts of the latter. Kaufmann and Hansen-Schmidt [51] found α,β-diiodoethylene to react rapidly with bromine in carbon tetrachloride in light, but not in darkness.

Schultze [52] briefly called attention to the possibility of a bromine-sensitization of the oxidation of unsaturated hydrocarbons.

The Action of Iodine on Unsaturated Hydrocarbons. Badger and Urmston [53] suggested the possibility of separating two types of iodine molecule, only one of which absorbs the 5461A line, by causing the activated type to react photochemically with hexene vapor.

The photosensitizing action of iodine upon the decomposition of ethylene iodide in carbon tetrachloride solution has been studied by Schumacher and Wiig.[54] The rate is proportional to the concentration of the ethylene iodide and to the square root of the absorbed light energy. At 100°C. the temperature coefficient is 1.57 per 10°. The mechanism involves a chain of simple type carried by iodine atoms. Murthi [55] finds their data consistent with every collision between iodine atoms in solution resulting in the formation of iodine molecules. According to Schumacher and Stieger [56] the quantum yield decreases markedly in the band region at 5461 or 5770A as compared with that at 4360A. Their results indicate that at 5460A and 5780A, excited iodine molecules for the most part give up their energy without dissociating. Murthi [57] calculates from their data and the assumption that every collision between iodine atoms produces a molecule, that the energy of activation is 12 kcals. as compared with an observed value of 11.8. No steric factor is needed to bring the calculated and observed rates into agreement. Dickinson and Nies,[58] objected that Schumacher's conclusion that excited molecules in the band region largely lose their energy without dissociating was the result of a failure to take into account possible variations in the absorption of the green and blue lines. They repeated rate measurements at various wave-lengths giving special consideration to the distribution of energy. As a result, they concluded that the rates are only slightly lower in the region of discontinuous absorption than in that of continuous absorption. The rate of the reaction depends only upon the rate of production of iodine atoms, irrespective of whether they are formed by primary dissociation or as a result of collisions of excited molecules, presumably with solvent molecules.

When an equimolar quantity of iodine was added to 0.01 molar solutions of 1-butene in methylene chloride or chloroform and the solutions illuminated, 90 per cent of the iodine disappeared in three hours in the former solvent at −60 to −90°C. and 98 per cent in the latter at −60 to −70°C.[59] On irradiating the solutions in quartz by a spark between high-tungsten steel electrodes, the iodine was evolved quantitatively within an hour in three stages. At 20°C. for 100 hours, 84 per cent of the iodine was evolved, also in stages.

In the quantitative photoiodination (4360, 5460, 6440A) of the first six simple

[51] Kaufmann, H. P., and Hansen-Schmidt, E., *Arch. Pharm.*, **263**, 32 (1925); *J. Chem. Soc.*, **128**, A*(II)*, 554.
[52] Schultze, G. R., *J. Am. Chem. Soc.*, **53**, 3561 (1931).
[53] Badger, R. M., and Urmston, J. W., *Proc. Nat. Acad. Sci.*, **16**, 808 (1930); *Chem. Abs.*, **25**, 1737 (1931).
[54] Schumacher, H. J., and Wiig, E. O., *Z. physik. Chem.*, **11B**, 45 (1930).
[55] Murthi, D. S. N., *J. Indian Chem. Soc.*, **12**, 173 (1935); *Brit. Chem. Abs.*, **A**, 832 (1935); *Chem. Abs.*, **29**, 5351 (1935).
[56] Schumacher, H. J., and Stieger, G., *Z. physik. Chem.*, **12B**, 348 (1931).
[57] Murthi, D. S., *J. Indian Chem. Soc.*, **12**, 173 (1935); *Chem. Abs.*, **29**, 5351 (1935).
[58] Dickinson, R. G., and Nies, N. P., *J. Am. Chem. Soc.*, **57**, 2382 (1935).
[59] Forbes, G. S., and Nelson, A. F., *J. Am. Chem. Soc.*, **58**, 182 (1936).

olefins at −55°C., the quantum yields vary as much as forty-fold. They fall off with decreasing frequency of light to the order of 0.01 at 6440A.[60] The rate is nearly proportional to the concentrations of olefins and of iodine, and to the light intensity. 1,2-Diiodobutane, prepared at low temperatures, was photolyzed at −60, −20 and 25°C., the quantum yields increasing from 0.7 to 1.15.

DeRight and Wiig [61] find that in red light, a solution of iodine and ethylene in carbon tetrachloride readily yields ethylene iodide, although no dark reaction occurs in 36 hours. The rate depends on the ethylene pressure and falls off with decreasing concentrations of iodine. The reaction probably involves excited iodine molecules. The photodecomposition yields iodine atoms, and the sensitized decomposition proceeds similarly.

The photochemical chlorination of acetylene has been investigated by Peters and Neumann [62] under a variety of conditions by static and dynamic methods. When mixtures of chlorine and acetylene at pressures up to 50 mm. were illuminated by a mercury arc, the pressure rose after a definite time, and then dropped suddenly, indicating the formation of $C_2H_2Cl_2$ and $C_2H_2Cl_4$. With higher proportions of acetylene, larger proportions of the former compound were obtained. An increase of 30 per cent in the time of illumination increased the chlorine consumption by 5 per cent. The percentage of contraction on illumination increased with the pressure. Pure nitrogen had little effect on the reaction, but nitrogen containing about 5 per cent of oxygen stopped it. In the presence of a large excess of hydrogen, a smaller yield was obtained but there was practically no formation of hydrogen chloride. The explosive process $C_2H_2 + Cl_2 \rightarrow 2C + 2HCl$ cannot occur at pressures below 70 mm.

The photobromination of acetylene, in which $C_2H_2Br_2$ is formed, has been studied at 150°C. by Booher and Rollefson,[63] using the wave-lengths 4358, 5461 and 5791A. It is a chain reaction with chain length of from about 500 at 150°C. to 3000 at 20°C. independent of the wave-length. The rate depends on the first power of the light intensity and on powers of the bromine and acetylene concentrations between zero and one. No difference is found in the effect of light of wave-lengths above and below the convergence limit of the bromine bands. The influence of temperature is very small.

These experiments were repeated by Franke and Schumacher,[64] who minimized the effects of impurities by using greaseless valves and measured the rate by a spiral quartz pressure gauge. Their results differed, but exact rate equations could not be given. The following reactions were suggested as playing a part in the mechanism:

$$Br_2 + h\nu \longrightarrow Br + Br.$$
$$Br + C_2H_2 \longrightarrow C_2H_2Br$$
$$C_2H_2Br \longrightarrow C_2H_2 + Br$$
$$C_2H_2Br + Br_2 \longrightarrow C_2H_2Br_2 + Br$$
$$C_2H_2Br \longrightarrow W \longrightarrow C_2H_2 + 1/2Br_2$$
$$Br \longrightarrow Wall \longrightarrow 1/2Br_2$$
$$Br + Br + M \longrightarrow Br_2 + M'$$

[60] Forbes, G. S., and Nelson, A. F., *J. Am. Chem. Soc.*, **59**, 693 (1937).
[61] DeRight, R. E., and Wiig, E. O., *J. Am. Chem. Soc.*, **58**, 693 (1936).
[62] Peters, K., and Neumann, L., *Angew. Chem.*, **45**, 261 (1932).
[63] Booher, J. E., and Rollefson, G. K., *J. Am. Chem. Soc.*, **56**, 2288 (1934).
[64] Franke, W. K., and Schumacher, H. J., *Z. physik. Chem.*, **B34**, 181 (1936); see, however, Rollefson, G. K., *Z. physik. Chem.*, **B37**, 472 (1937).

Higher quantum yields (40,000) have since been found at 90°C. and with 100 mm. pressure of each of the reactants.[65]

The bromination of acetylene bromide, by wave-lengths 5460, 4360 and 4060A, is thirty times as fast in the gas phase as in solution in carbon tetrachloride under equivalent conditions.[66] In both cases, the unimolecular rate constant for the removal of bromine is proportional to the square root of the absorbed energy. The temperature coefficient is 1.4.

Ghosh and Bhattacharya extend the work to include the iodination of phenylacetylene, dicyclopentadiene and β-amylene.[67]

Other Aliphatic Compounds

Volmar[68] claimed that methyl sulfate readily undergoes chlorination at ordinary temperatures under the influence of ultraviolet rays and more slowly under the influence of the light from an arc lamp or a metal filament lamp, the product in all cases being methyl chloromethyl sulfate. The fixation of a second chlorine atom was not observed. It was thought to require radiations of such a wave-length that the dichloromethyl sulfate would be decomposed as it formed.

The bromination of ethyl alcohol occurs under the influence of light.[69] The reaction is retarded by potassium bromide. A satisfactory mechanism has not yet been proposed. Berthoud believes C_2H_5O may function as an intermediary. In the case of propyl, isopropyl and butyl alcohols the quantum yields are large (5660, 6800 and 8500A).[70] They increase with temperature and decrease with increasing wave-lengths. The rate of the reaction increases with the amount of light energy-absorbed. At these longer wave-lengths the primary reaction is believed to be the activation of bromine molecules. The temperature coefficients were found to be above two in most cases. With Bhagwat, Malaviya and Dhar[71] found the rate of the reaction with propyl alcohol to be proportional to the square root of the light intensity at 6800A and nearly so at 8500A, but directly proportional to it at 5660A. On the other hand, with isopropyl and butyl alcohols, the rates were proportional to the square root at 6800A and directly proportional to it at 5600 and 8500A. In all cases the reaction is retarded by potassium bromide, and the rates are then proportional to the square roots of the intensities.

The rate of addition of iodine to allyl alcohol in aqueous solution is not influenced by light, but with carbon tetrachloride as solvent there is a photochemical reaction similar to the photobromination.[72]

Monochloropinacolone has been prepared by treating pinacolone in carbon tetrachloride with chlorine in a quartz flask exposed to strong ultraviolet light.

[65] Müller, K. L., and Schumacher, H. J., *Z. physik. Chem.*, **B39**, 352 (1938); **B40**, 318 (1938).

[66] Ghosh, J. C., Bhattacharya, S. K., and Bhattacharya, S. C., *Z. physik. Chem.*, **B32**, 145 (1936). For the bromination of dichloroacetylene, Ghosh, J. C., Bhattacharya, S. K., and Murthi, M. L. N., *J. Indian Chem. Soc.*, **14**, 425 (1937); *Brit. Chem. Abs.*, **AI**, 627 (1937).

[67] Ghosh, J. C., and Bhattacharya, S. K., *Science and Culture*, **3**, 120 (1937); *Chem. Abs.*, **32**, 414 (1938).

[68] Volmar, *Bull. soc. chim.*, **27**, 181 (1920); *J. Chem. Soc.*, **118**, (I), 661 (1920); *Chem. Abs.*, **14**, 3406 (1920).

[69] Bugarski, S., *Z. physik. Chem.*, **71**, 705 (1910); Berthoud, A., and Béraneck, J., *J. chim. phys.*, **25**, 28 (1928).

[70] Malaviya, K. N., and Dhar, N. R., *Z. anorg. allgem. Chem.*, **199**, 418 (1931); *Chem. Abs.* **25** 5846 (1931).

[71] Bhagwat, W. V., Malaviya, K. N., and Dhar, N. R., *Z. anorg. allgem. Chem.*, **199**, 406 (1931); *Chem. Abs.*, **25**, 5846 (1931).

[72] Berthoud, A., and Mosset, M., *J. chim. phys.*, **33**, 272 (1936).

[73] Hill, G. A., and Kropa, E. L., *J. Am. Chem. Soc.*, **55**, 2509 (1933).

It is a highly lachrymatory ketone.[73] Hill and Kropa also find that colorless monobromopinacolone, when exposed for six hours to ultraviolet light, becomes yellow and then orange. Most of the material is unchanged but some dibromopinacolone can be obtained.

Acids and Their Salts. In the manufacture of lethal gases in Germany during the war, Carr[74] states, the preparation of diphosgene proved very troublesome. Methyl formate was chlorinated in vessels furnished with chlorine pipes and carefully lined first with lead and then with two layers of tiles. The cement was said to consist of powdered fireclay, asbestos and sodium silicate. These precautions were necessary because any metal introduced onto the mixture from the reaction vessel acts as an anticatalyst. The temperature had to be carefully controlled during the reaction to obtain the best results. As a source of light, which was necessary, an Osram lamp of 4000 c.p. was used. The reaction took from six to eight days for completion.

In the process of chlorination of methyl chloroformate described by Kling, Florentin, Lassieur and Schmutz,[75] methyl chloroformate is first prepared by the action of carbonyl chloride on methyl alcohol at as low a temperature as possible, a small amount of dimethyl carbonate being formed as a by-product. No matter whether the chlorination takes place in sunlight, arc light, or the light of an incandescent lamp, the monochloroester is obtained almost free from the dichloro-compound which, having almost the same boiling point, is very difficult to remove. Further chlorination gives the dichloroester which is easily fractionated from the trichloroester which is also formed. Chlorination to the limit gives the latter. Methyl formate may also be used as the starting material, giving practically the same products.

Grignard, Rivat and Urbain[76] state that chlorination of methyl chloroformate in diffused light gives only the chloromethyl ester, and that bright sunlight is necessary for the formation of the di- or trichloromethyl ester. In ultraviolet rays, the trichloromethyl ester is easily obtained. The effect of temperature is such that up to 110-112°C. the chlorination proceeds smoothly; from 113-114°C., it slackens very noticeably. At 117°C. decomposition begins to take place, with the formation of carbonyl chloride. Catalysts, such as ferric chloride, antimony chloride, etc., are initially beneficial in the formation of dichloromethyl ester, but when a certain concentration has been reached, decomposition commences, and may continue indefinitely, since some of the perchloride becomes dissolved in the liquid and continues its action.

Formic acid itself is chlorinated with quantum yields of about 2000 when the 3650A mercury lines are employed. These lines do not affect the acid but only the chlorine in the primary process. West and Rollefson[77] find evidence for the production of an unstable intermediary product, chloroformic acid. If this is destroyed by heat or if there is an excess of chlorine, hydrochloric acid and carbon dioxide are the only products. There is no appreciable difference in reactivity between the single and double molecules of formic acid. For the former the reactions involved may be:

[74] Carr, F. H., *J. Soc. Chem. Ind.*, **38**, 468R (1919).

[75] Kling, A., Florentin, D., Lassieur, A., and Schmutz, R., *Compt. rend.*, **169**, 1046 (1919); *Chem. Abs.*, **14**, 738 (1920).

[76] Grignard, V., Rivat, G., and Urbain, E., *Compt. rend.*, **169**, 1074, 1143 (1919); *J. Chem. Soc.*, **118**, 1138 (1920).

[77] West, H. L., and Rollefson, G. K., *J. Am. Chem. Soc.*, **58**, 2140 (1936).

$$Cl_2 + h\nu \longrightarrow Cl + Cl$$
$$Cl + HCOOH \longrightarrow COOH + HCl$$
$$COOH \longrightarrow CO_2 + H$$
$$COOH + Cl_2 \longrightarrow ClCOOH + Cl$$
$$H + Cl_2 \longrightarrow HCl + Cl$$
$$ClCOOH \longrightarrow CO_2 + HCl$$
$$Cl + Cl + M \longrightarrow Cl_2 + M$$

A similar mechanism can be given for the reaction with the double molecules.

In the chlorination of acetic acid in a quartz flask under the influence of rays from an iron arc, Custis [78] found that the yield of monochloracetic acid is improved by the use of red phosphorus as a catalyst. No reaction was observed when the light from an ordinary projection lantern replaced the iron arc. No results were obtained by passing the chlorine gas through a quartz tube irradiated with ultraviolet light before passing it into a non-irradiated flask containing glacial acetic acid.

Benrath and Hertel found that acetyl chloride and isobutyric acid behave similarly to acetic acid. With propionic acid and with ethyl malonate, the reaction commenced slowly and then continued at a rate proportional to the time until one atom of hydrogen had been replaced. The second atom then reacted at a much slower rate and in accordance with the logarithmic law. Two atoms of hydrogen were replaced in *n*-butyric acid, both at logarithmic rates, the steps of the reaction being markedly distinct. The chlorination of ethyl ether proceeded linearly during the displacement of one atom and then, after slowing up, the second atom was replaced at a logarithmic rate. The induction period was long in the case of acetic anhydride and the reaction was in two phases, but the rates were neither linear nor logarithmic. Some of the results indicated a tendency toward periodicity.[79]

In the photobromination of lactic acid, Ghosh and Basu [80] found it impossible to get regular values for a monomolecular rate constant. It appeared that the quantum yield was low, about 0.25, but the measurements were not considered very accurate since about two-thirds of the transformation appeared to be due to the thermal reaction. Much more regular results were obtained in the case of calcium lactate, but even in this case the dark reaction accounted for about 75 per cent of the observed velocity. Increasing the concentration of the salt increased the velocity constant, but increasing the bromine concentration made the constants irregular, the reaction tending to degenerate into one of zero order. When the concentration of the salt is small ($0.03N$), the quantum yield is about 0.5, but this becomes unity when the concentration is increased to $0.06N$.[81]

Purkayastha [82] finds that in the bromination of organic acids, there is an induction period which vanishes in the presence of potassium bromide. The quantum yields, higher than those of other observers, possibly because of elimination of oxygen, are for light of 4700A, 15 (lactic acid), 13 (phenyl-lactic acid), 13 (mandelic acid) and 3 (citric acid). The induction period is ascribed to the formation of complexes between bromine and the reacting acid. The velocity constants vary inversely with the square root of the incident intensity of the blue light. At 5420, 4880, 4480, 4080 or 3650A, the order is zero molecular.

[78] Custis, H. H., *J. Frank. Inst.*, **184**, 874 (1917); see also Benrath, A., and Hertel, E., *Z. wiss. Phot.*, **23**, 30 (1924).

[79] See, however, Plotnikow, J., *Z. wiss. Phot.*, 2379 (1924).

[80] Ghosh, J. C., and Basu, K., *Quart. J. Indian Chem. Soc.*, **2**, 39 (1925); *Chem. Abs.*, **20**, 43 (1926).

[81] For temperature coefficients in various solvents, see Yajnik, N. A., and Uppal, H. L., *J. Indian Chem. Soc.*, **6**, 729 (1929); *Chem. Abs.*, **24**, 1035 (1930).

[82] Purkayastha, R. M., *J. Indian Chem. Soc.*, **6**, 361, 375, 385 (1929); **7**, 991 (1930); *Chem. Abs.*, **23**, 5420 (1929); **24**, 784 (1930); **25**, 2922 (1931).

In the case of the bromination of tartaric acid in aqueous solution, the Indian workers [83] found an induction period of two days. The unimolecular rate constant decreased as the initial concentration of bromine was increased, and increased with that of tartaric acid, the more so when part of the acid was replaced by the acid salt. It diminished when hydrobromic acid was added before exposure, decreased with time and increased rapidly with increase in frequency of light employed. It varied approximately as the square root of the light intensity. The quantum yield was high, bromine atoms being involved in the mechanism. These reacted with oxygen (present in solution or liberated by the photochemical reaction of bromine molecules with water) at a rate directly proportional to the oxygen concentration and to the square of the bromine atom concentration. Photoinhibitors were also destroyed by reacting with bromine atoms. The temperature coefficient of the velocity is high, 4.6 per 10°C.

Prik [84] chlorinated impure methyl stearate in diffused light without a catalyst until it contained 2.5 atoms of chlorine per molecule. When heated to 100°C. with zinc dust, this product split off 12 per cent of its chlorine.

The reactions of bromine and of iodine with oxalic acid have been discussed in Chapter 22. In the case of the chlorination by wave-lengths 4650, 5650, and 7304A, Bhattacharya and Dhar [85] find the temperature coefficients to be 2.3, 2.4 and 2.5. The quantum yields are 8.6, 7.2 and 4.9, there being little difference in the reaction as conducted by absorption in the band or continuous spectral regions. In a later reinvestigation of this reaction, they, with Mukerji,[86] concluded that in the absence of potassium iodide the thermal and the photochemical reactions are uni- and semi-molecular, respectively. The reaction rate is not a constant function of the light intensity. Stirring increases the rate and reduces the temperature coefficient, which is the smaller the greater the acceleration due to light.

The addition of bromine to maleic and fumaric acids is not influenced by light, according to Berthoud and Mosset.[87]

When bromine was added to β-phenylpropiolic acid in cold chloroform and the reaction allowed to go to completion at room temperature in light, the *cis-trans* ratio in the products was about two to one. In darkness at zero, it was three to two. With the methyl ester, the ratios were one to three and one to two, respectively.[88]

In preparing α-bromo-β-methoxybutyric acids, West and Carter brominate in sunlight an addition product of crotonic acid and mercuric acetate.[89]

Cyclic Compounds. Mono- and di-brom-phenylcyclopropane-1,2-dicarboxylic acids were prepared by Haerdi and Thorpe [90] by using the rays of a powerful arc lamp. Nicolet and Sattler [91] found that bromine reacts easily with ethyl-

[83] Ghosh, J. C., and Mukherjee, J., *Quart. J. Indian Chem. Soc.*, **2**, 165 (1925); *Chem. Abs.*, **20**, 870 (1926); Ghosh, J. C., and Basu, K., *J. Indian Chem. Soc.*, **5**, 343, 361 (1928); *Chem. Abs.*, **22**, 4379 (1928).

[84] Prik, E. M., *Plasticheskie Massui*, **6**, 26 (1934); *Chem. Abs.*, **29**, 4734 (1935); see also Scheibler, H., and Schmidt, H. J., *Ber.*, **69B**, 12 (1936).

[85] Bhattacharya, A. K., and Dhar, N. R., *J. chim. phys.*, **26**, 556 (1929).

[86] Bhattacharya, A. K., Dhar, N. R., and Mukerji, B. K., *J. Indian Chem. Soc.*, **12**, 151 (1935); *Brit. Chem. Abs.*, **1935A**, 832.

[87] Berthoud, A., and Mosset, M., *J. chim. phys.*, **33**, 272 (1936).

[88] Ayyar, P. R., *J. Indian Inst. Sci.*, **18A**, 123 (1935); *Chem. Abs.*, **30**, 2185 (1936).

[89] West, H. D., and Carter, H. E., *J. Biol. Chem.*, **119**, 103 (1937).

[90] Haerdi, W., and Thorpe, J. F., *J. Chem. Soc.*, **127**, 1237 (1925).

[91] Nicolet, B. H., and Sattler, L., *J. Am. Chem. Soc.*, **49**, 2069 (1927).

cyclopropane-1,1-dicarboxylate even in diffused light. The nature of the product depended on the conditions of bromination. Apparently both ethyl 2-bromocyclopropane-1,1-dicarboxylate and β-bromoethylbromomalonate were formed in all cases, but the proportion of the latter was much higher when the bromination was carried out at higher temperatures and under mercury-arc illumination. The former is apparently the primary product from which the latter is produced by subsequent reaction of the hydrobromic acid liberated. Bromination of cyclopropane-1,1-dicarboxylic acid in carbon tetrachloride in ultraviolet light affords bromo-β-bromoethylmalonic acid. In chloroform, the product is a viscous oil, which loses carbon dioxide upon distillation with the formation of 2-bromocyclopropane-carboxylic acid. Bromination of ethyl 1-cyanocyclopropane-1-carboxylate affords ethyl 2-bromo-1-cyancyclopropane-1-carboxylate and ethyl α,γ-dibromo-α-cyanobutyrate. Bromine is without action in ultraviolet light on cyanocyclopropane and 1-cyanocyclopropane-1-carboxylic acid.

The photobromination of cyclohexane by rays of wave-length 5460A at 30°C. has been investigated by Wood and Rideal.[92] Both the thermal and the photochemical reactions conform to the unimolecular law and the latter has no temperature coefficient. The velocity of the reaction is proportional to the light intensity, independent of the cyclohexane concentration and reduced by the presence of oxygen, the inhibition by the latter being independent of the pressure of the cyclohexane. Jost[93] found the characteristics of the reaction to be the same in both the regions of continuous and discontinuous absorption by the halogen. The reaction constant varied approximately with the square root of the cyclohexane concentration. The temperature coefficient was two and the quantum yields increased with rising temperatures.

In carbon tetrachloride, the chlorination of this compound under the influence of either white or monochromatic light, is unimolecular with respect to chlorine. The velocity coefficient is directly proportional to the intensity of the incident radiation, independent of the concentration of chlorine and increases slightly with the concentration of the cyclohexane.[94] The coefficient diminishes a little as the reaction proceeds, apparently because of the retarding influence of the chlorcyclohexane formed. The quantum efficiency is 19 at 4360A, 30 at 4040A and 41 at 3660A. The temperature coefficients for these wave-lengths are 1.5, 1.29 and 1.26, respectively.

Aromatic Compounds

The influence of light in facilitating the chlorination of toluene in the side-chain has long been known and employed in practice. Before discussing this reaction and its application, attention will be devoted to the halogenation reactions of benzene.

Luther and Goldberg[95] found the frequently irregular course of the photochlorination of benzene to be due to the retarding effect of small quantities of oxygen, an effect frequently noted in chlorination reactions in general. The rate of the reaction with liquid benzene is proportional to the square of the pressure of the chlorine employed. The final product seems to be largely benzene hexachloride.[96]

On the other hand, in the vapor phase the reaction proceeds by a *short*-chain

[92] Wood, B. J., and Rideal, E. K., *J. Chem. Soc.*, 2466 (1927).
[93] Jost, W., *Z. physik. Chem., Bodenstein Festschrift*, 291 (1931).
[94] Basu, K. P., *J. Indian Chem. Soc.*, **6**, 691 (1929); *Chem. Abs.*, **24**, 1033 (1930).
[95] Luther, R., and Goldberg, E., *Z. physik. Chem.*, **56**, 43 (1906); *J. Chem. Soc.*, **90**, *(II)*, 641 (1906).
[96] Slator, A., *Z. physik. Chem.*, **45**, 540 (1903).

mechanism.[97] It was found that the main initial reaction is one of addition but that some substitution also occurs. At the beginning, the rate of change of pressure is proportional to the square root of the light intensity and to the pressure of the chlorine and that of the benzene. No pressure change is observed unless phenyl chloride forms and condenses on the wall. After this there is a liquid reaction which consists in large part in the addition of chlorine to benzene dissolved in the liquefied phenyl chloride.

In the gas phase photochlorination of chlorobenzene, which also proceeds by short chains, the initial rate of reaction of the chlorine is proportional to a power of the light intensity between 0.5 and 1.0. The rate is also about proportional to the product of the chlorine and chlorobenzene concentrations and is increased by surfaces. The ratio of substitution to addition increases from much less than one to more than one as the ratio of chlorine used to the initial pressure of chlorobenzene increases. The rate of addition of chlorine to *p*-dichlorobenzene is slightly less than that to chlorobenzene. Some intermediate substances have been isolated; the final product is dodecachlorocyclohexane.

There is little difference in the rates of photochemical chlorination of the three dichlorobenzenes.[98] The rate is proportional to the light intensity at low intensities but at higher ones depends on some power between 0.5 and 1.0. It is independent of the chlorine pressure except as this affects the light absorption, but is proportional to the pressure of dichlorobenzene.

The rate of addition of liquid chlorine to three trichlorobenzenes in sunlight at room temperature has been found by van der Linden[99] to decrease in the order of the 1,2,3-, 1,2,4- and 1,3,5- compounds, requiring 7 days, 10 days and 9 weeks, respectively. The first gives only one isomer of 1,1′,2,2′,3,3′,4,5,6-nonachlorocyclohexane, of musty camphor-like odor, m.p. 80°C. The second gives a series of mixed crystals of two isomers of $C_6H_3Cl_9$ and 1,2,2′,3,4,4′,5,6-octachloro-6-cyclohexene, obtained by the loss of hydrogen chloride from a third unstable isomer. The 1,3,5-trichlorobenzene yields one isomer of 1,1′,2,3,3′,4,5,5′,6-nonachlorocyclohexane. Addition is assumed to occur most readily at double linkings unsubstituted in both Kekule forms. Van der Linden also reports[100] on the addition of chlorine to penta- and hexachlorobenzene. The former yielded hexachlorobenzene and a mixture of 1,2,3,3′,4,4′,5,6,6′-*ennea*chloro-1-cyclohexene and its stereoisomer. The hexachlorobenzene gave dodecachlorocyclohexane and a small quantity of decachlorocyclohexene.

The β-isomer of hexachlorobenzene after 17 days in sunlight, formed principally β-*p*-dichlorobenzene hexachloride and probably the 1,2,4-trichlorine derivative.[101]

Hexabromodihydrobenzene and liquid chlorine, exposed to sunlight for 40 days in a sealed tube, gave dodecachlorohexane, $C_6H_2C_{12}$, melting 108-110°C.[102]

The liquid phase photobromination of benzene in carbon tetrachloride by low concentrations of bromine (1 to 2 mg. per cc.) has been studied by Meidinger.[103] The bromine can either be directly substituted in the ring with the formation of monobromobenzene, or the double bonds may be broken with the formation of

[97] Lane, C. E., Jr., and Noyes, W. A., Jr., *J. Am. Chem. Soc.*, **54**, 161 (1932); Smith, H. P., Noyes, W. A., Jr., and Hart, E. J., *Ibid.*, **55**, 4444 (1933); Hart, E. J., and Noyes, W. A., Jr., *Ibid.*, **56**, 1305 (1934).
[98] Fisk, C. F., and Noyes, W. A., Jr., *J. Am. Chem. Soc.*, **58**, 1707 (1936).
[99] van der Linden, T., *Rec. trav. chim.*, **55**, 315 (1936); *Chem. Abs.*, **30**, 6345 (1936).
[100] van der Linden, T., *Rec. trav. chim.*, **55**, 569 (1936); *Chem. Abs.*, **30**, 7103 (1936).
[101] van der Linden, T., *Rec. trav. chim.*, **57**, 217 (1938); *Chem. Abs.*, **32**, 4542 (1938).
[102] van der Linden, T., *Ibid.*, **57**, 401 (1938); *Chem. Abs.*, **32**, 5775 (1938).
[103] Meidinger, W., *Z. physik, Chem.*, **5B**, 29 (1929); *Z. Elektrochem.*, **35**, 738 (199).

benzene hexabromide. The reaction is independent of the bromine concentration and of the wave-length of light used. Meidinger was unable to explain his observation that the temperature coefficient decreased from 1.6 to 1.0 as the concentration of benzene employed decreased.

Rabinowitsch [104] also found the temperature coefficient 1.6; it varied but little with the light intensity or the wave-length between 3000 and 5500A. There was, however, a fall with wave-lengths approaching the convergence limit of bromine and an increase with increasing concentrations of the latter. The quantum yield at room temperature was 0.4 to 0.9. This author believed that even when the solution was considerably diluted with solvent, the bromine molecules remained attached to the benzene molecules and on light absorption reacted with them. The compound $C_6H_6Br_6$ may be formed chiefly by the reaction of activated bromine molecules, but the phenyl bromide results from a reaction with bromine atoms:

$$C_6H_6 + Br \longrightarrow C_6H_5 + HBr$$
$$C_6H_5 + Br_2 \longrightarrow C_6H_5Br + Br.$$

The first of these requires thermal activation and accounts for the high temperature coefficient of the photochemical reaction and the lessening of the coefficient on dilution.

In a sealed tube exposed to light, phenyl fluoride and liquid chlorine react vigorously, yielding in a day a few crystals, possibly 1-fluoro-1,2,3,4,4′,5,6-heptachlorocyclohexane [105] and an oil which on steam distillation yielded a volatile oil, $C_6H_5FCl_6$, and a non-volatile residue, probably a mixture of isomers of this composition. Under similar conditions, phenyl bromide liberated bromine and hydrogen chloride and formed a chlorobromobenzene hexachloride. Phenyl iodide reacted much more slowly; among the products isolated after several weeks were C_6ICl_5, *p*-ClC_6H_4I and probably 2,4,5-trichloroiodobenzene.

Toluene. According to Book and Eggert,[106] toluene, chlorinated by a stream of chlorine at 105° to 110°C., yields almost exclusively benzyl chloride, irrespective of whether the reaction is carried out in light or in darkness, provided a chlorine "carrier," *e.g.*, ferric chloride, is not present. In the presence of such a "carrier," however, considerable amounts of *o*- and *p*-chlorotoluene are produced. At −80°C. a photochemical reaction occurs in the absence of a carrier as a result of absorption of the orange and light green mercury lines, with a quantum yield of about 25. The initial reaction probably comprises the formation of hydrogen chloride together with chlorotoluene or benzyl chloride.

The influence of light on the chlorination of toluene has been the subject of several early patents.[107]

In the laboratory of the senior author,[108] a number of experiments have been made to compare the production of benzyl chloride, benzal chloride and benzotrichloride under various conditions. The best results were obtained by passing an excess of toluene vapor mixed with chlorine through a transparent quartz tube at variously elevated temperatures and exposed to ultraviolet radiations. The product was withdrawn from the reaction tube and the contents collected and fractionated; the unused toluene was returned through the reaction tube. In order to determine the effect

[104] Rabinowitsch, E., *Z. physik. Chem.*, **19B** 190 (193).

[105] van der Linden, T., *Rec. trav. chim.*, **55,** 282 (1936); *Chem. Abs.*, **30,** 5192 (1936).

[106] Book, G., and Eggert, J., *Z. Elektrochem.*, **29,** 521 (1923); *Ber.*, **59B,** 1192 (1926); *Chem. Abs.*, **18,** 668 (1924); See also Bergel, F., *Ber.*, **59B,** 153 (1926); *Chem. Abs.*, **20,** 1602 (1926).

[107] See, *e.g.*, Ransford, R. B., British P. 16,317, July 8, 1914; *J. Soc. Chem. Ind.*, 1203 (1915).

[108] Ellis, Carleton, U. S. P. 1,202,040, Oct. 24, 1916; for a special form of chlorination chamber, Ellis, Carleton, U. S. P. 1,146,142, July 13, 1915.

of ultraviolet rays on this reaction the source of the rays was removed and the experiment carried out in a similar manner. The results of one test are given in Table 22.

Table 22.—Products from Chlorination of Toluene.

Fraction	Quartz Tube without Ultraviolet (per cent)	Quartz Tube with Ultraviolet (per cent)
Up to 150°C.	72	42
150-170°C.	4.2	2.
170-185°C.	18.5	47.5
185-215°C.	3.8	6.5

A process for the manufacture of side-chain chlorinated toluene advocated by Gibbs and Geiger,[109] called for ultraviolet radiation. It was claimed that when toluene in vapor phase is mixed with chlorine gas in the definite theoretical proportions to produce chlorinated side-chain products and the mixture exposed to ultraviolet rays, the bodies desired are produced in greatly increased yields and without the production of interfering by-products. By carefully regulating the speed at which the reacting substances pass continuously through the reaction chamber, a high degree of purity results. They state that it is advisable to work without a catalyst since it is not essential to the reaction and would tend to contaminate the products. According to this process, benzyl chloride, benzal chloride and benzotrichloride may be produced in accordance with the proportion of chlorine employed. Gibbs [110] states that when a low-pressure mercury-vapor lamp is used, a mixture of benzyl chloride and benzal chloride is produced and that a high-pressure mercury-vapor lamp gives benzotrichloride. Conklin [111] has patented sectional glass reaction towers for the chlorination of benzene or toluene under the influence of actinic rays. However, the use of ultraviolet rays is not essential.[112]

In experiments on the photobromination of toluene, made in atmospheres of 96 per cent and 4 per cent nitrogen, LeBlanc and Andrich [113] found the yield of benzyl bromide independent of the intensity of light and constant throughout the entire portion of the spectrum investigated. The speed of the reaction decreased with decrease of wave-length and was practically zero for wave-lengths shorter than 3000A. Swensson [114] reports that the rate of absorption of bromine by toluene and xylene in the presence of alcohol and when exposed to the rays of a quartz mercury arc at 20°C. is retarded, owing to the ability of alcohol to remove the hydrogen bromide, which catalyses the reaction, at the same time being itself decomposed. Kharasch, White and Mayo [115] believe that in light the yield of the side-chain bromination reaction is lowered when oxygen is partly excluded. They consider it a chain reaction carried by bromine atoms, the source of which may be hydrogen bromide when oxygen or oxygen carriers are present.

Natelson [116] obtained an 85-per cent yield of $C_6H_5CHClCH_3$ based on the

[109] Gibbs, H. D., and Geiger, G. A., U. S. P. 1,246,739, Nov. 13, 1917; Canadian P. 186,466, Sept. 10, 1918.

[110] Selden Co. and Gibbs, H. D., British P. 123,341, Oct. 22, 1927; *Chem. Abs.*, **13,** 1478 (1919); *J. Soc. Chem. Ind.*, **38,** 268A (1919).

[111] Conklin, E. P., U. S. P. 1,828,859, Oct. 27, 1931, to Solvay Process Co.; *Chem. Abs.*, **26,** 632 (1932).

[112] Silberrad, O., and Boake, A., [British P. 259,329, July 22, 1925; *Chem. Abs.*, **21,** 3370 (1927)] chlorinated organic compounds with sulfuryl chloride in the presence of catalysts such as chlorides of phosphorus, manganese, arsenic, selenium, antimony, bismuth, molybdenum, and the chlorides of iron, sulfur and aluminum. Actinic light may be used.

[113] LeBlanc, M., and Andrich, K., *Z. Elektrochem*, **20,** 543 (1914).

[114] Swensson, T., *Z. wiss. Phot.*, **20,** 206 (1921); *J. Chem. Soc.*, **120,** II, 291 (1921).

[115] Kharasch, M. S., White, P. C., and Mayo, F. R., *J. Org. Chem.*, **3,** 33 (1938).

[116] Natelson, S., *Ind. Eng. Chem.*, **25,** 1391 (1933).

chlorine employed from ethylbenzene in the light of an S-1 sun-lamp. Evans, Mabbott and Turner[117] found chlorination of pure ethylbenzene in diffused daylight to yield a mixture of α- and β-phenylethylchlorides, increased illumination increasing the proportion of the former. In experiments of Varma, Sahay and Subramonium,[118] the addition of eight drops of nitrosulfonic acid and two cc. of bromine in ten cc. of acetic acid to ten cc. of ethylbenzene in bright sunlight yielded a small quantity of 4-bromoethylbenzene and four grams of α-bromoethylbenzene. The former product was obtained in greater yield in the absence of light. Bromination of ten cc. of 4-chloroethylbenzene in bright sunlight produced seven cc. of 4-chloro-α-bromoethylbenzene.

Intense visible light causes a rapid reaction between cyclopropane and bromine vapor. About two per cent of the bromine reacted appears as hydrogen bromide. The main product is $BrCH_2CH_2CH_2Br$.[119]

For the laboratory-scale preparation of *m*-xylylchloride by the chlorination of *m*-xylene with the production of as little 4-chloro-1,3-dimethylbenzene as possible, King and Merriam[120] developed a chlorinator made from a 500-cc. distilling flask and a Pyrex tube connected to a reflux condenser. It was illuminated by a 400-watt nitrogen-filled lamp while 260 gms. of *m*-xylene was boiled in the flask. Chlorine (126 gm.) was passed in at the rate of 40 gms. per hour through a 0.5 mm. tube directly into the current of vapor. 17 gms. of *m*-xylene was found remaining in the hydrogen chloride absorbers and 305 gms. of product was in the flask. As a result of very careful fractionation, 68.79 gms. of *m*-xylene was recovered and 20.20 gms. of 4-chloro-1,3-dimethylbenzene and 190.83 gms. of *m*-xylyl chloride were obtained. In the presence of oxygen, chlorination was extremely slow.

The influence of ultraviolet radiation, in the presence and absence of catalysts, on the reactivity of halogen bound to a carbon ring, has been investigated by Rosenmund, Luxat and Tiedemann.[121] The comparative inertness of a halogen in an aromatic compound is overcome in the presence of copper at 180 to 220°C. At somewhat lower temperatures, the radiation from a quartz mercury-vapor lamp has a decidedly accelerating effect on the reaction

$$ClC_6H_4COOH + KOH \longrightarrow HOC_6H_4COOH + KCl$$

in the absence of copper and is still more active in its presence. At 104°C., the radiation is still an accelerating agent, but the copper is inactive.

According to Olivier,[122] when *p*-chlorobenzene sulfochloride in ethereal solution is exposed to direct sunlight or to the rays of a Uviol lamp, chlorine is liberated and oxidation takes place with the formation of the free sulfonic acid. When the experiment is carried out by passing dry oxygen through the ethereal solution of the sulfochloride while exposed to the rays of the lamp, the quantity of chlorine collected shows a deficit when compared with the equivalent of sulfonic acid formed; aldehyde and hydrochloric acid are found in the aqueous liquid on treatment with water. It is probable, therefore, that some of the chlorine reacts with the ether to form chloroethyl ether, which is subsequently hydrolyzed to

[117] Evans, E. B., Mabbott, E. E., and Turner, E. E., *J. Chem. Soc.*, 1159 (1927).
[118] Varma, P. S., Sahay, V., and Subramonium, B. R., *J. Indian Chem. Soc.*, **14**, 157 (1937); *Chem. Abs.*, **31**, 7411 (1937).
[119] Ogg, R. A., Jr., and Priest, W. J., *J. Am. Chem. Soc.*, **60**, 217 (1938).
[120] King, H. S., and Merriam, M. K., *Proc. Nova Scotian Inst. Sci.*, **18**, 276 (1933-4); *Chem. Abs.*, **29**, 6214 (1935).
[121] Rosenmund, K. W., Luxat, K., and Tiedemann, W., *Ber.*, **56B**, 1950 (1923); *Chem. Abs.*, **17**, 3837 (1923).
[122] Olivier, S. C. J., *Rec. trav. chim.*, **36**, 117 (1916); *J. Soc. Chem. Ind.*, **35**, 1149 (1916).

aldehyde. Under favorable conditions, the decomposition of the sulfochloride under the influence of light and oxygen amounts to over 40 per cent in six hours, and the reaction is practically inhibited in the absence of light or oxygen and a peroxide may play a part in the reaction. The presence or absence of moisture has no appreciable influence. The photochemical decomposition of the sulfochloride is considerable in ethereal solution but only slight in chloroform. In benzene and carbon tetrachloride, the reaction does not take place. Other sulfochlorides of the benzene series behave in a similar manner but to a lesser degree.

Schmitz and Co.[123] have prepared esters of phenol homologs halogenated in the side-chain by treating the esters alone or in suitable solvents, such as carbon tetrachloride, with halogen in the presence of light, especially from a source rich in ultraviolet rays.

Jenkins[124] employs a 500-watt tungsten lamp in the conversion of ketones of the type $R'.CH_2COR$ and $R.CH_2COR'$ into α-bromo- derivatives such as $R'CHBrCOR$ and $RCHBrCOR'$. Feist[125] finds that *p*-acetyltoluene in the light of a mercury lamp at 100 to 110°C. adds six atoms of chlorine, forming *p*-trichloroacetyl trichloromethyl benzene. According to Connerade,[126] the chlorination of dimethylbenzophenone first at 120°C. and then at 140°C., yields, besides products chlorinated in the ring, $(Cl_2CHC_6H_4)_2CO$, a liquid freezing to a crystalline paste at about 0°C. It is very sensitive to light, which transforms it into a plastic mass.

According to I. G. Farbenindustrie,[127] 2,5-dimethyl-4-chlorobenzophenone may be chlorinated by trichlorobenzene at 170-180°C. while being exposed to the action of a mercury-vapor lamp to give an ω-hexachloro- derivative.

Van der Linden[128] has obtained, after chlorination of benzoic acid in sunlight, a γ- and a β-hexachloride, a pentachlorocyclohexene carboxylic acid and a mixture which, when distilled in steam, yielded the first two of these, the α-isomer, 1,2,4,5-tetra-, penta- and hexachlorobenzene and pentachlorocyclohexene carboxylic acid.[129] He found also that benzoyl chloride and chlorine in sunlight slowly gave a mixture of equal parts of δ-1,2,3,4,5,6-hexachlorocyclohexane carboxylchloride and β-1,2,3,4,5,6,4′-heptachlorocyclohexane carboxylchloride, a γ-isomer of the δ-compound, an α-isomer of the β-compound and an oil which, after treatment with dilute alkali and steam distillation yielded a little 1,2,4,5,-tetrachlorbenzene, three isomeric hexachlorocyclohexenes, a mixture of $C_6H_{11}COOH$ and $HOC_6H_4Cl_6COOH$ or of $HOC_6H_5Cl_5COOH$ and $C_6H_5Cl_6COOH$, the acid of the δ-carboxylchloride and ε-benzoic acid hexachloride.

Perkin and Stone[130] find that when 2,4-dimethyl benzoyl chloride is brominated at 160°C. by the aid of a mercury lamp, the bromo-acid bromide distilling at 169-171°C. at 15 mm., consists mainly of 2-bromomethyl 4-methyl benzoylbromide, $CH_3C_6H_3(CH_2Br)COBr$, but the fraction 160-180°C. at 15 mm., contains this substance and 4-bromomethyl 2-methylbenzoyl bromide, $CH_2BrC_6H_3CH_3COBr$, in the proportion of about 85 to 15 per cent. When 2,4-dimethylbenzoyl chloride is treated with a calculated amount of chlorine for the introduction of three atoms, at a temperature rising from 180 to 210°C. and in ultraviolet light, and the product is distilled, a fraction is obtained boiling 184-186°C. (16 mm.), the

[123] British P. 3053, Feb. 5, 1914, to Schmitz and Co.
[124] Jenkins, S. S., *J. Am. Chem. Soc.*, **56**, 682 (1934).
[125] Feist, F., *Ber.*, **67B**, 938 (1934).
[126] Connerade, E., *Bull. soc. chim. Belg.*, **43**, 447 (1934); *Chem. Abs.*, **29**, 768 (1935).
[127] British P. 394,990, June 29, 1933, to I. G. Farbenind. A.-G.; *Chem Abs.*, **28**, 176 (1934).
[128] van der Linden, T., *Rec. trav. chim.*, **53**, 703, 779 (1934); *Chem. Abs.*, **28**, 5425 (1934).
[129] See also for the chlorination of aromatic carboxylic acids in sunlight, Feist, F., German P. 563,129, May 21, 1930, to I. G. Farbenind. A.-G.
[130] Perkin, W. H., Jr., and Stone, J. F. S., *J. Chem. Soc.*, **127**, 2275 (1925).

chlorine content of which corresponds to that of the expected ω-trichloro-2,4-dimethyl benzoyl chloride. It was found, however, that this fraction was in reality an almost constant boiling mixture of di- and tetra-chlorinated dimethyl-benzoyl chloride. When the chlorination was continued in ultraviolet light until the increased weight corresponded to the introduction of four atoms of chlorine, and the product fractionated, 2,4-di(dichloromethyl)benzoyl chloride, boiling at 192-193°C. (10 mm.) was obtained in good yield. An acid chloride fraction boiling 188-192°C. (14 mm.) was obtained when chlorine was passed into 2,4-dimethyl benzoyl chloride in the presence of ultraviolet light at 200°C. until the increase in weight corresponded to the absorption of five atoms of chlorine. The product contained about equal quantities of the isomeric chlorides, $CCl_3C_6H_3(CHCl_2)COCl$ and $CHCl_2(CCl_3)COCl$. It was also possible to obtain the chloride of 2,4-di(trichloromethyl)benzoic acid by chlorinating at 220°C. in ultraviolet light until six chlorine atoms were absorbed. The yield was 70 to 80 per cent.

The bromination of salicyclic acid to the dibromo- derivative occurs slowly in carbon tetrachloride either in daylight or darkness, and more rapidly in methyl alcohol; but exposure to daylight or to the light of a mercury-vapor lamp scarcely accelerates the reaction.[131]

Austin and Bousquet[132] cause phthalide to react with a rapid flow of chlorine in ultraviolet light at 130-140°C. with vigorous agitation, until approximately 0.75 atom of chlorine per molecule is absorbed. The chlorination product, on hydrolysis with boiling water, followed by cooling, filtering and recrystallizing from benzene, yields phthaldehydic acid. Similarly, a 5-nitro- acid may be formed from 5-nitro-phthalide.

Matthews, Bliss and Elder[133] have found that styrolene may be prepared from β-bromohydrocinnamic acid by the action of steam, by a silent electric discharge or by ultraviolet rays.

In the bromination of stilbene in carbon tetrachloride, the velocity coefficient is independent of the concentration of the bromine, but increases as the initial concentration of the stilbene increases. The temperature coefficient is 2.6. The quantum yield is 305 molecules of stilbene dibromide per absorbed quantum.[134]

In direct sunlight or artificial light (but not in darkness in the absence of peroxidic substances), a solution of isostilbene in benzene is transformed by the action of hydrogen bromide into stilbene in about five minutes. The reaction is prevented by antioxidants. It cannot be effected by the use of hydrogen chloride.[135]

According to Ghosh and Basu,[136] the photobromination of ethyl *m*-nitrobenzylidene malonate to the dibromide in carbon tetrachloride solution is reversible. The equilibrium constant varies with the intensity of the light. A rise in temperature causes a slight increase in the concentration of the dibromide. The velocity of the direct action is not affected by the concentration of ester, bromine or dibromide. With Bhattacharya, these authors[137] found an analogous behavior in carbon disulfide, but the values for the equilibrium constant were but one-seventh of those

[131] Kaufmann, H. P., and Hansen-Schmidy, E., *Archiv Pharm.*, **263,** 32 (1925).

[132] Austin, P. R., and Bousquet, E. W., U. S. P. 2,047,946, to E. I. du Pont de Nemours & Co.; *Chem. Abs.*, **30,** 6011 (1936); *Brit. Chem. Abs.*, **B,** 879 (1937).

[133] Matthews, F. E., Bliss, H. J. W., and Elder, H. M., British P. 16,828, July 22, 1913.

[134] Ghosh, J. C., and Purkayastha, R. M., *J. Indian Chem. Soc.*, **2,** 261 (1925); **4,** 553 (1927); *Chem. Abs.*, **20,** 1953 (1926); **22,** 4379 (1928). See also Kato, S., *Bull. Inst. Phys.-Chem. Research (Tokyo)*, **11,** 765 (1932); *Chem. Abs.*, **26,** 5260 (1932). Quite different results have been reported by Berthoud[138] and coworkers.

[135] Kharasch, M. S., Mansfield, J. V., and Mayo, F. R., *J. Am. Chem. Soc.*, **59,** 1155 (1937).

[136] Ghosh, J. C., and Basu, K. P., *J. Indian Chem. Soc.*, **4,** 375 (1927); *Brit. Chem. Abs.*, **1928 AI,** 176.

[137] Bhattacharya, S. C., Ghosh, J. C., and Basu, K. P., *J. Indian Chem. Soc.*, **5,** 183 (1928); *Brit. Chem. Abs.*, **1928A,** II, 757.

in the former solvent. The velocity of the initial stage was proportional to the concentration of bromine and increased considerably with increase in concentration of the ester.

The rate of the addition in chloroform, measured under conditions in which the back reaction is negligible, follows the same laws as the photobromination of cinnamic acid and stilbene.[138]

Tetrachloroarsine, $RAsX_4$, was found by Hamilton and King[139] to decompose into RX and AsX_3 under the influence of ultraviolet light at temperatures of 75 to 120°C. At temperatures around 100°C. the orange-colored 4-methyl phenyl-tetrachloroarsine suddenly decomposed into *p*-chlorotoluene and arsenic trichloride after having been exposed to the radiations for about two hours. With continued chlorination at the same temperature and in the presence of ultraviolet light, there was a rapid gain in weight, indicating that the *p*-chlorotoluene was being chlorinated. Use may be made of the ability of ultraviolet light to break an arsenic-to-carbon linkage in determination of the structure of more complex arsenicals. It was found in the case of *p*-toluene arsenic acid that chlorine substituted in the nucleus and not in the sidechain. In order to prove the position of the chlorine in the ring the arsenic acid was converted into the corresponding tetrachloroarsine, the arsenic-to-carbon linkage broken by the action of chlorine under the influence of ultraviolet light, and the dichlorotoluene thus formed was chlorinated and hydrolyzed to yield 2,4-dichlorobenzoic acid.

Halogenation of Other Types of Compounds

Ultraviolet light has been suggested as an aid in the preparation of chloronaphthalene.[140] According to Davies and Oxford,[141] 4,1-nitromethyl naphthalene and bromine when exposed in a quartz flask to ultraviolet light give a yellow monobromo- derivative, melting at 137.5 to 138.5°C. and a very small quantity of a tetrabromo- derivative, melting at 189 to 190°C. The bromination of naphthalene is a unimolecular reaction having a temperature coefficient of 1.57 per ten degrees between 5 and 30°C., according to Kozak and Pazdor.[142] The velocity for a given rate of absorption of energy is greatest in blue light. The velocity of photobromination of various methyl and ethyl derivatives of naphthalene has also a maximum in blue light, but with the bromine substitution reactions of these substances, and also of toluene, there is a secondary maximum in the yellow range.

1,5-dibenzoyl-2,6-dimethyl, 1,5-di(*o*-chlorobenzoyl) and 1,5-di(2,5-dichlorbenzoyl)-2,6-dichloronaphthalene are chlorinated at from 160 to 200°C. with a finely divided stream of chlorine in the light of a mercury lamp to give the ω-hexachloro- derivative. The products are condensed by treatment with concentrated sulfuric acid.[143]

Chlorination of 2-methyl-α-naphthoyl chloride at 150 to 170°C. under the influence of arc lamp irradiation, and hydrolysis of the resulting product with water and calcium carbonate forms β-naphthylaldehyde-1-carboxylic acid.[144]

[138] Berthoud, A., and Mosset, M., *J. chim. phys.*, **33,** 272 (1936).

[139] Hamilton, C. S., and King, W. N., *J. Am. Chem. Soc.*, **55,** 1689 (1933).

[140] Ellis, C., and McElroy, K. P., U. S. P. 914,251, March 2, 1909; *Chem. Abs.*, **3,** 1447 (1909).

[141] Davies, J. S. H., and Oxford, A. E., *J. Chem. Soc.*, 220 (1931).

[142] Kozak, J., and Pazdor, F., *Bull. Akad. Polonaise*, **A,** 477, 489 (1933); *Chem. Abs.*, **28,** 4114 (1934).

[143] British P. 427,327, April 23, 1935, to I. G. Farbenind. A.-G.; *Chem. Abs.*, **29,** 5866 (1935).

[144] Mayer, F., Schäfer, W., and Rosenbach, J., *Arch. Pharm.*, **267,** 571 (1929); *Brit. Chem. Abs.*, **1928A,** 1294.

Tatum and Thomson [145] prepare α-halogenated anthraquinones by halogenating in the sun, or other actinic light, anthraquinone or its halogenated derivatives capable of further α-halogenation, in the presence or absence of halogen carriers, solvents or diluents. Thus anthraquinone is chlorinated in oleum in the presence of iodine under the action of sunlight, 1,4,5,8-tetrachloroanthraquinone being obtained. This, treated with phthalimide, and hydrolyzed to the tetra-amino-derivative, yields dyes which turn blue.

Phenanthrene can be brominated only by a light reaction.[146]

Terpenes. Cineole, in carbon tetrachloride solution, has been chlorinated in sunlight by Gandini,[147] who obtained a mono- and a di-chloro- derivative. Although light is indispensable for the formation of the mono-chloro- derivative, the reaction is slower and the yields are lower in ultraviolet light. In later work,[148] there was obtained from 100 gms. of cineole, 15 gms. of a mixture of 2-chlorocineole and 3-chlorocineole, 80 gms. of dichloroisomers, 25 gms. of a trichloro- derivative and 25 gms. of undistilled residue. A still higher percentage of chlorine led to more extensive chlorination and to products which could not be separated. Separation of the dichloroisomers yielded 2,3-dichlorocineole, an oil which slowly turns pale yellow on exposure to light.

Passage of chlorine into cumene containing 15 per cent acetic acid in sunlight affords *p*-chlorocumene and 1,3-dichloro-2-phenylpropane, the relative yields depending on the light intensity.[149]

Pseudocumene can be brominated by mixing with bromine and exposing to sunlight for about three hours.[150] The products formed depend upon the nature of the subsequent heating. If the exposed mixture is heated on a water-bath only the monobromide is obtained, but if it is heated to 170°C., a mixture of mono-, di- and tribromides results; the relative proportions depend upon the amount of bromine used. A mixture of 5-bromopseudocumene and bromine exposed to sunlight for three hours and heated for three hours gave di- and tri-nuclear substituted bromine derivatives in fairly good yields. In Bruylants's method for the preparation of trimethylene chlorobromide, allyl chloride is saturated with hydrobromic acid in sunlight. Strukov [151] finds the yield 95-97 per cent.

In direct sunlight in chloroform, camphane reacts immediately with chlorine with evolution of hydrogen chloride. The product yields bornyl chloride, which, treated in direct sunlight with chlorine in ice-cold carbon tetrachloride, yields a mixture of various halogenated derivatives difficult to separate. Gandini [152] was able to obtain 2,3-dichlorocamphane, melting at 126-126.5°C., a trichloro- derivative, melting at 130-2°C., and other unidentified compounds.

Diphenosuccindan-9,12-dione in carbon tetrachloride may be brominated in the light of an arc lamp to the 10-bromo- compound.[153]

Light has no influence on the chlorination of lignin.[154] On the other hand, chlorination of wool is slower in diffused light than in direct light.[155]

[145] Tatum, W. W., and Thomson, R. F., British P. 364,141, Sept. 2, 1930; *Chem. Abs.*, **27**, 1640 (1933).
[146] Kharasch, M. S., White, P. C., and Mayo, F. R., *J. Org. Chem.*, **2**, 574 (1938).
[147] Gandani, A., *Gazz. chim. ital.*, **63**, 151 (1933); *Chem. Abs.*, **27**, 3707 (1933).
[148] Gandani, A., *Gazz. chim. ital.*, **64**, 118 (1934); *Chem. Abs.*, **28**, 4723 (1934).
[149] Varma, P. S., and Srinivasan, M. K., *J. Indian Chem. Soc.*, **13**, 189 (1936); *Chem. Abs.*, **30**, 5949 (1936); see also Qvist, W., and Salo, A., *Acta Acad. Aboensis, Math. Phys.*, **8**, 4 (1934); *Chem. Abs.*, **29**, 6884 (1935).
[150] Varma, P. S., and Sen-Gupta, D. N., *J. Indian Chem. Soc.*, **11**, 351 (1934); *Chem. Abs.*, **28**, 6119 (1934).
[151] Strukov, I., *Khim. Farm. Prom.*, **2**, 66 (1933); *Brit. Chem. Abs.*, **A**, 55 (1934).
[152] Gandini, A., *Gazz. chim. ital.*, **66**, 357 (1936); *Chem. Abs.*, **31**, 2595 (1937).
[153] Brand, K., Gabel, W., Ott, H., Müller, K., and Fleischhauer, R., *Ber.*, **69B**, 2504 (1936).
[154] Sarkar, P. B., *J. Indian Chem. Soc.*, **11**, 777 (1934); *Chem. Abs.*, **29**, 2514 (1935).
[155] Utaka, S., *Reports Imp. Ind. Research Inst. Osaka, Japan*, **15**, 11 (1935); *Chem. Abs.*, **29**, 2751 (1935).

Part III

Applications of Photochemistry to Industrial Products

Chapter 29

Reactions of Fatty Acids. The Preservation of Foods

In discussing the effects of light on the production of rancidity in foods, attention is first directed to the photochemistry of the fatty acids since these, when present as esters in fats and oils, are primarily responsible for the changes which occur.

It has been reported that acids with carbon chains longer than C_2, both saturated and unsaturated, become ketonic on exposure to light, atmospheric oxygen favoring the reaction.[1] The passage of air in the presence of tropical sunlight through solutions of potassium stearate, palmitate or oleate, according to Palit and Dhar,[2] is accompanied by oxidation, which increases with the intensity of the light. Zinc oxide is an effective photosensitizer.

The rate of oxygen consumption by undecenic acid, decenic acid, oleic acid and olive oil in light is greatly increased by the addition of very dilute solutions of chlorophyll or eosin as sensitizers, the former being ten times as effective as the latter. Hemin does not act as a sensitizer, at least for the oxidation of decenic and undecenic acids.[3] In the case of oleic acid, hydroxyoleic acid is formed. In general, there seemed to be no destruction of double bonds in these experiments.

Täufel and Seuss [4] found that the oxygen absorption, peroxide formation and epihydrinaldehyde formation in a highly purified sample of oleic acid was affected by light in the same manner as by the addition in darkness of such catalysts as ferrous, ferric or cupric chlorides. Custis [5] found the hydrogenation of oleic acid to be unaffected by ultraviolet radiations from an iron arc. A copper-egg white complex also catalyzes the oxidation of unsaturated fatty acids; this effect may be increased five to ten times by irradiation of the complex.[6]

Linoleic acid takes up oxygen and forms peroxides by a photochemical chain reaction.[7] The rate of peroxide formation is independent of the oxygen concentration and temperature and proportional to the concentration of acid and to the square root of the light intensity. As steps in the mechanism the following reactions were suggested (A is linoleic acid and M solvent):

$$A + h\nu \longrightarrow A^*$$
$$A^* + O_2 \longrightarrow AO_2^*$$
$$AO_2^* + A \longrightarrow A^* + AO_2$$
$$AO_2^* + M \longrightarrow M^* + AO_2$$
$$M^* + A \longrightarrow M + A^*.$$

[1] Schmallfuss, H., Werner, H., and Gehrke, A., *Margarine Ind.*, **26**, 3, 87 (1933); *Brit. Chem. Abs.* **B**, 416 (1935).

[2] Palit, C. C., and Dhar, N. R., *J. Phys. Chem.*, **32**, 1263 (1928).

[3] Meyer, K., *J. Biol. Chem.*, **103**, 597 (1933). Certain porphyrins also inhibit the autoxidation of a mixture of linoleic and linolenic acids in sodium cholate solutions at pH 7.12. The inhibitors may be destroyed by ultraviolet irradiation. Hinsberg, K., and Ammon, R., *Z. physiol. Chem.*, **246**, 139 (1937).

[4] Täufel, K., and Seuss, A., *Fettchem. Umschau*, **41**, 107, 131 (1934); *Chem. Abs.*, **29**, 370 (1935).

[5] Custis, H. H., *J. Frank. Inst.*, **184**, 880 (1917).

[6] Kather, E., *Arch. exptl. Path. Pharmakol.*, **184**, 645 (1937); *Chem. Abs.*, **32**, 8448 (1938).

[7] Horio, M., *Mem. Coll. Eng. Kyoto Imp. Univ.*, **8**, No. 18, 26 (1934); *Chem. Abs.*, **28**, 5338 (1934); Horio, M., and Monden, S., *J. Soc. Chem. Ind. Japan*, **37**, 488B (1934); *Chem. Abs.*, **29**, 52 (1935); Horio, M., and Yamashita, S., *J. Soc. Chem. Ind. Japan*, **37**, 392, 416 (1934); *Chem. Abs.*, **28**, 7165 (1934).

Light rays shorter than 4000A are effective, ordinary sunlight having only a few suitable wave-lengths for oxidative action.

These observers also found that in the absence of oxygen the light of a mercury arc caused a bleaching of mixtures of aqueous solutions of linoleic acid with alcoholic solutions of eosin, Victoria Violet or erythrosin (but not Victoria Blue, which is non-fluorescent) more rapid than in darkness. The dye is reduced and the acid oxidized. The bleaching of the dye was less rapid when oxygen was bubbled through the solutions.

The rate of bromination of oleic, linoleic and linolenic acids is in inverse ratio to the number of double bonds they contain,[8] oleic acid acting the most and linolenic acid the least rapidly. Under the influence of ultraviolet light the bromination of both the so-called "pure" acids and the mixed fatty acids proceeds further than in darkness. This was held to indicate the presence of unsaturated isomers not revealed by the usual analytical methods.

As in the case of other unsaturated compounds, stereoisomeric transformations and polymerization reactions occur during irradiation. The former have been relatively little studied; the latter are discussed particularly in the following chapter.

Irradiation of "iodostarin" (di-iodide of tariric acid) in chloroform by sunlight, mercury-vapor light or Osram light, causes its dissociation into tariric acid and iodine.[9]

$$CH_3-(CH_2)_{10}\cdot CI=CI\cdot(CH_2)_4COOH \rightleftarrows CH_3-(CH_2)_{10}\cdot C\equiv C\cdot(CH_2)_4COOH+I_2$$

At room temperatures, the change is reversible and follows the law of mass action, but at higher temperatures there are deviations from this behavior. The equilibrium is independent of the strength of the light, but the rates of reaction are directly proportional to it. Since it was found that this decomposition is caused by the rays absorbed by the iodine, the photolysis must be regarded as sensitized by iodine.

Ultraviolet light promotes the formation of a diricinoleic acid by the condensation of the hydroxyl group of one molecule of ricinoleic acid with the carboxyl group of another.[10]

Lederer[11] investigated the effect of small concentrations of metals on the color of a two-to-one mixture of stearic and oleic acids in darkness, after eight hours in direct sunlight and after two hours of exposure at 40 cm. from an ultraviolet source. During neither of these exposures did manganese, aluminum, zinc or lead produce a color change. The presence of 0.04 per cent. nickel led to a slight yellowing in sunlight but there was no color change after ultraviolet irradiation. Samples with 0.04 per cent copper exhibited distinct yellowing, and those containing iron showed considerable darkening, the effect being more pronounced in sunlight than in ultraviolet light. Samples lacking metallic adulteration were scarcely affected. It was concluded that the discoloration of fats after manufacture is primarily dependent upon the presence of traces of iron and copper.

Triglycerides are said to be hydrolyzed in the presence of water by the action of ultraviolet rays.[12]

[8] Knauss, C. A., and Smull, J. G., *J. Am. Chem. Soc.*, **49**, 2808 (1927).

[9] Baur, E., *Helv. Chim. Acta*, **18**, 1149 (1935); *Chem. Abs.*, **30**, 28 (1936).

[10] Zlatarov, A., and Bieliavski, V., *Ann. univ. Sofia, Faculte phys.-math.*, **28**, No. 2, 21 (1932); *Chem. Abs.*, **28**, 3054 (1934).

[11] Lederer, E. L., *Z. angew. Chem.*, **42**, 1033 (1929); *Seifensieder Ztg.*, **56**, 278 (1929); *Chem. Abs.*, **24**, 741 (1930).

[12] Tern, R., German P. 357,695; *J. Soc. Chem. Ind.*, **41**, 945A (1922).

DuNoüy[13] has called attention to a slight decrease in the surface tension of dilute sodium oleate solutions after three hours of exposure to light. Mahajan[14] attributes it to a chemical change which is most marked when ultraviolet light is used. The effect is at a maximum in soap solutions of 6.25×10^{-4} gm. per cc.[15]

Oils

Absorption and Fluorescence. The absorption of oils depends upon that of the acids they contain. In the case of cod-liver and other fish oils the well-defined absorption bands are due to sites of unsaturation. The highly absorbing acids obtained from them by saponification are apparently not, however, straight-chain compounds with conjugated double bonds since their absorption may be increased by prolonging the time of the saponification,[16] or by conducting it at elevated temperatures.[17] During this process cyclization probably occurs with the formation of hydroaromatic polycyclic products.

Considerable attention has been devoted to the absorption of fish-liver oils in connection with work on the distribution of vitamins A and D therein. (See Chapter 41.)

Of the vegetable oils studied, linseed oil shows the greatest absorption, according to Harvey,[18] who used an actinometric method which did not permit determination of the wave-length distribution of the absorption. Lewkowitsch[19] measured the absorption of thin films of whale, herring, olive, teaseed and linseed oils. Both the animal and vegetable oils gave curves of the same type, absorption gradually increasing toward the shorter wave-lengths. The feeble absorption bands superposed upon the more or less general absorption could not, however, be used for the purpose of determining individual oils in mixtures. Although Lewkowitsch found in some samples of olive oil indications of a band at 2750A, Lundé, Kringstad and Weedon[20] showed that the value of the extinction coefficient at this wave-length characterizes various samples of this oil. In virgin olive oil it was 10 to 22, in refined pressed oil 35-55 and in refined extracted oil 54-90. Two unrefined extracted oils, however, gave values of 80 and 120.[21]

The blue fluorescence follows the same trend. Cortese[22] has shown that the examination of the fluorescence of various samples of olive oils cannot distinguish natural (yellow) from refined oil (blue in general), since the addition of chlorophyll or carotene to refined oils imparts to them the fluorescence characteristic of expressed oils. It may be possible to remove this by animal charcoal. Fixed oils from damaged fruit behave like refined oils. Fixed oils from olives stored only two or three days also fluoresce blue-violet.[23]

[13] DuNoüy, P. L., *Nature*, **131**, 689 (1933).

[14] Mahajan, L. D., *Z. Physik*, **98**, 388 (1935).

[15] Acidity developed in a saturated mineral oil when exposed to sunlight or ultraviolet light is believed by Woog, P., [*Compt. rend.*, **189**, 977 (1929)] to affect its spreading on solid surfaces.

[16] Dann, W. J., and Moore, T., *Biochem. J.*, **27**, 1166 (1933).

[17] Edisbury, J. R., Morton, R. A., and Lovern, J. A., *Biochem. J.*, **27**, 1451 (1933); **29**, 899 (1935).

[18] Harvey, E. H., *J. Am. Pharm. Assn.*, **19**, 1173 (1930); **20**, 643 (1931).

[19] Lewkowitsch, E., *J. Soc. Chem. Ind.*, **46**, 195T (1927).

[20] Lundé, G., Kringstad, H., and Weedon, H. W., *Angew. Chem.*, **46**, 796 (1933); Kringstad, H., *Angew. Chem.*, **49**, 423 (1936); Moore, T., *Biochem. J.*, **31**, 38 (1937).

[21] See also Rousseau, E., *Compt. rend. soc. biol.*, **96**, 611 (1927); *Chem. Abs.*, **21**, 1933 (1927).

[22] Cortese, D., *Industria chimica*, **9**, 1048 (1934); *Chem. Abs.*, **28**, 7044 (1934); Walter, C., *Olii minerali, olii e grassi, colori e vernici*, **15**, 149 (1935); *Chem. Abs.*, **31**, 6041 (1937); Fachini, S., and Martinenghi, G., *Olii minerali, olii e grassi, colori e vernici*, **17**, 54 (1937); *Chem. Abs.*, **32**, 3647 (1938).

[23] Ciusa, W., *Olii minerali, grassi e saponi, colori e vernici*, **18**, 33 (1938); *Chem. Abs.*, **32**, 8178 (1938).

Fluorescence colors excited by ultraviolet light have also been frequently suggested as aids in the identification of other fats and oils. Haitinger, Jorg and Reich [24] recorded the fluorescence colors of a number of oils and fats for use in the detection of adulterants in butter, cacao butter, lard, olive oil, etc. Butter is said [25] to give a golden yellow color, but margarine and synthetic fats appear grayish white. It is claimed that 20 per cent of foreign fat may easily be detected in this manner. Solid or molten lards [26] generally give a slight bluish fluorescence, but no definite conclusions may be drawn from its color as to the origin of the sample. Applied microscopically, the method may be used for distinguishing between shell and nib tissue in cocoa.[27] The brilliant white luminescence of cacao butter in the light of a quartz lamp is, according to Mauersberger,[28] due to traces of aluminum and calcium soaps formed while in contact with fullers' earth during bleaching. It is not characteristic of extracted butter because any pressed butter similarly treated with fullers' earth would give it.

Much attention has been devoted to the property possessed by seeds and oils of affecting a photographic plate as does light. Stutz, Nelson and Schmutz [29] believed it due to the evolution of hydrogen peroxide. The effect is greatly increased by exposure of the oils to light. Since only the unsaturated acids isolated from the oil, and not the saturated ones, are effective, the phenomenon appears to be associated with the drying of the oil. de Loureiro [30] attributed the effect to the evolution of ozone. The vapor from the oil must be brought in contact with the photographic plate.[31] Ried [32] believed that the effect in various fats parallels their ability to form vitamin D on irradiation. This has been much discussed, but at present is regarded as merely an incidental phenomenon. Irradiation does not affect the electrical conductivity of cod-liver oil.[33]

Photochemical Changes of Various Edible Oils. Wall [34] subjected cacao oil to the action of ultraviolet rays to destroy its objectionable taste and odor.

The bleaching of palm oil by light may be sensitized by the addition of various dyestuffs added to aqueous emulsions of the oil. Baur and Fabbricotti [35] estimated that the quantum yields when various dyes are employed is low, of the order of 10^{-3}. Exposure of olive oil to ultraviolet radiation for an hour has been found to cause an increase of more than 5 per cent in the acidity.[36] After exposure for about a week a comparatively rapid air-drying has been observed.[37] During exposure to ultraviolet, radium or x-rays, the dielectric constant, acid number and iodine number are the constants of olive oil which undergo the greatest change.[38]

Sun rays bleach layers of olive oil from 1 mm. to 1000 mm. in thickness,

[24] Haitinger, M., Jorg, H., and Reich, V., *Z. angew. Chem.*, **41**, 815 (1928); Kaufmann, H. P., *Chem. Umschau Fette, Oele, Wachse, Harze*, **36**, 34 (1929); *Chem. Abs.*, **23**, 2051 (1929); Déribéré, M., *Mat. grasses*, **29**, 246, 279 (1937).

[25] Novacek, E., and Hokl, J., *Z. Fleisch. Milchhyg.*, **42**, 47 (1932); *Chem. Abs.*, **26**, 2881 (1932).

[26] Braunsdorf, K., *Z. Unters. Lebensm.*, **63**, 407 (1932); *Chem. Abs.*, **27**, 785 (1933).

[27] Wasicky, R., and Wimmer, C., *Z. Nahr. Genussm.*, **30**, 25 (1915).

[28] Mauersberger, E. A., *Chem. Ztg.*, **56**, 861 (1932).

[29] Stutz, G. F. A., Nelson, H. A., and Schmutz, F. C., *Ind. Eng. Chem.*, **17**, 1138 (1925).

[30] de Loureiro, A. J., *Compt. rend. soc. biol.*, **96**, 1321, 1324 (1927); *Chem. Abs.*, **21**, 2484 (1927).

[31] Hopwood, F. L., and Mayneord, W. V., *Nature*, **116**, 98 (1925).

[32] Ried, O., *Wien. klin. Woch*, **42**, 1105 (1929).

[33] Butler, L. W., and Woodrow, J. W., *Iowa State Coll. J. Sci.*, **11**, 333 (1937); *Chem. Abs.*, **32**, 4722 (1938).

[34] Wall, E. J., U. S. P. 1,386,476, Aug. 2, 1921; *Chem. Abs.*, **15**, 3913 (1921).

[35] Baur, E., and Fabbricotti, G. F., *Helv. Chim. Acta*, **18**, 7 (1935).

[36] Lesure, A., *J. pharm. chim.*, **7**, 575; *Chem. Abs.*, **5**, 963 (1911).

[37] Eibner, A., and Rasquin, H., *Chem. Umschau*, **33**, 29 (1926); *Chem. Abs.*, **20**, 2422 (1926).

[38] Kovalev, T. G., *Isvestiya Zentral. Nauch Issledovatelskog Inst. Pishchevoi Vkussovoi Prom., U.S.S.R.*, 3, (1931); *Chem. Abs.*, **26**, 5222 (1932).

but the thicker the layer the slower the action.[39] For quick bleaching a maximum contact of oil, air and sunlight is needed. With oil flowing slowly down low steps, bleaching occurs in half the time. The bleaching does not completely destroy the fluorescence observed on exposure of the oil to Wood's light. Thirty days of exposure produced but little change in most of the constants, contrary to the observations of others on the effects of ultraviolet. Thus, the acidity was unchanged, the iodine number increased from 81.9 to 82.8, the refractive index changed from 1.46588 to 1.46625 and the saponification number decreased from 193.5 to 191.9. The density increased from 0.9170 to 0.9175.

Putland [40] observed a more rapid bleaching of vegetable oils in the light of Mazda lamps than in sunlight. Ultraviolet from a quartz mercury arc, however, darkened instead of bleaching both cottonseed and soybean oils. Crude cottonseed oil, one inch in depth, exposed in a tin tray at 27°C. to the mercury-vapor light, darkened from 35 yellow, 7.9 red (Lovibond scale) in eight hours to 35 yellow, 8.3 red. A bleached cottonseed oil changed in ten hours from 20 yellow, 2.1 red to 20 yellow, 3.0 orange.

In the laboratory of the senior author numerous experiments on the bleaching and polymerization of various oils by a Cooper-Hewitt quartz mercury arc have been made.[41] Samples of crude cottonseed oil, linseed oil, crude whale oil (No. 3) and a strongly fluorescent medium-body lubricating oil were exposed in shallow pans in three-sixteenth inch layers at about eleven inches from the lamp. After three hours the linseed oil had a very heavy film, the cottonseed and whale oils slight films but the lubricating oil was unaltered. After six hours the cottonseed oil had greatly increased in viscosity, the linseed and whale oil had commenced to gelatinize and the lubricating oil had become slightly darker. After 13½ hours, the cottonseed oil had gelatinized and was slightly bleached. The linseed oil had become a stiff jelly and its odor was diminished, but the color was apparently unchanged. The whale oil was considerably deodorized and slightly bleached. The lubricating oil had become somewhat darker, but the fluorescence had completely disappeared.

With exposures closer to the lamp, the whale oil gave a dark, amber-colored jelly with a very faint odor as compared with that of the original oil. Crude cottonseed oil also gave a stiff amber-colored jelly, which was considerably lighter than the original oil. The iodine value had fallen to 56. A highly refined cottonseed oil, however, gave a jelly which in color and consistency could scarcely be distinguished from that of the crude oil. The temperature during irradiation was about 110°C. The crude sample fumed slightly during the exposure to ultraviolet but the refined oil did not fume below 160°C. and then but slightly. Crude oil polymerizes and gelatinizes more rapidly than refined oil. Special experiments in sealed tubes showed that the thickening and polymerization occurs even in the absence of oxygen. In its presence, however, the solidification of unsaturated fatty oils appears to be due jointly to oxidation and polymerization. In one experiment made at a distance of but four inches from the source, a layer of cottonseed oil commenced to thicken immediately and at the end of fourteen minutes had completely solidified to a very thick jelly. A thicker layer (one and a half inches) at four inches from the lamp had become a solid, dark-colored jelly after 7½ hours.

Castor oil after 10½ hours at three inches gave a product identical in appearance and odor with that obtained from cottonseed oil. Red oil (crude oleic acid) fumed slightly at 85°C. and copiously at 110°C. A thin surface film appears to protect the under layer from further action until it is removed. When completely solidified it is hard without any tackiness, black and odorless. A highly refined corn oil gave in 14 hours at four inches a jelly of a very light yellow color, the change occurring very gradually. Immediately before the viscous mass commences to solidify, a large number of small bubbles usually appear below the surface and could be still observed even after the oil had become completely solid. In one case a mixture of equal parts of rosin and corn oil became extremely viscous and somewhat darkened after five hours. The carbonizing

[39] Loew, G., *Olii minerali, olii grassi, colori vernici*, **12**, 89 (1932); *Chem. Abs.*, **26**, 6168 (1932).

[40] Putland, A. W., *Cotton Oil Press*, **7**, No. 7, 36 (1923).

[41] Ellis, Carleton, U. S. P. 1,089,359, March 3, 1914. Note also 1,179,414 and 1,180,025.

or discoloring action when very close to the rays was repeatedly noted. It may be partly due to a local superheating of the under layers of the oil.

In one case ordinary cottonseed oil was mixed with 5 per cent of sulfur and exposed to the action of ultraviolet for three hours at 150°C. It remained liquid after treatment. On the other hand, an oil which had been exposed until it was practically at the gelatinization point and then treated with the same amount of sulfur, on further exposure yielded a black, rubber-like solid. Stamberger[42] stated that vulcanized triolein, which is soluble in acetone and benzene, after treatment with sunlight or ultraviolet light is converted into a solid mass of molecular weight over 7000, insoluble in these and other organic solvents and swelling in benzene. Applications to the making of artificial rubber latex for impregnating textiles and making varnishes have been suggested.[43] Ellis also observed that an oil which had been hydrogenated to a titer of 54°C., after an exposure of three hours to ultraviolet light remained unchanged in color, odor and viscosity.

Early attempts to use ultraviolet light in aiding the reaction of catalysts in the hydrogenation of oils do not seem to have been successful.[44]

It has been suggested that the presence of unhydrogenated oils in hydrogenated products may be qualitatively detected by taking advantage of the fact that the former are darkened and polymerized by ultraviolet light while the latter are unaffected. An exposure of several hours is required.[45]

Oxidation of Oils. Much attention has recently been devoted to studies of the oxidation of oils, particularly in regard to the light it throws upon the production of rancidity in foods on storage. Ultraviolet light has a powerful effect upon the susceptibility of cottonseed oil to oxidation.[46] This change depends, according to Greenbank and Holm,[47] upon reactions occurring prior to the period of active oxidation.

During the absorption of small quantities of oxygen oxides and peroxides are believed to be formed; these are sometimes termed "moloxides" of the unsaturated acids. They alter the oxidation-reduction potential in a manner which may be followed by the aid of methylene blue or other indicators. The reduction of this indicator when dissolved in an unsaturated oil is rapid in strong sunlight. By using a 100-watt Mazda lamp as a constant source, the rate of the change in the color of the indicator, followed photoelectrically, affords an indication of the susceptibility of the oil to undergo the changes which lead to rancidity. Horio[48] measured the rate of the reaction by determining the concentrations of peroxides formed during ultraviolet irradiation of oils while oxygen was bubbled through them. With linseed oil and linoleic acid the rates were independent of the time of irradiation, proportional to the concentration of acid or oil, independent of temperature and oxygen concentration and proportional to the square root of the light intensity. With olive oil, the rate decreased with time to a constant value. The rate-intensity curve for this oil showed a maximum. Certain substances (vanillin, jara-jara, *p*-nitraniline) accelerate the formation of peroxides in ultraviolet light but not in darkness in linseed oil.[49] Irradiation also accelerates the effects of manganese and lead abietates.

[42] Stamberger, P., *Rec. trav. chim.*, **46**, 837 (1927); **47**, 973 (1928); Knight, B., and Stamberger, P., *J. Chem. Soc.*, 2794 (**1928**).

[43] Stamberger, P., and Auer, L., British P. 321,693, 1928; *Brit. Chem. Abs.* **B**, 652 (1930).

[44] Walter, H., *Seifensieder-Ztg.*, 442 (1913); cited by Ellis, C., "Hydrogenation of Organic Substances," 3rd ed., Van Nostrand, 1930; A mercury-sensitized process has been described by Karagunis, G., *Praktika Akad. Athenon*, **11**, 404 (1936); *Chem. Abs.*, **32**, 1580 (1938).

[45] Ellis, C., and Wells, A. A., *Chem. Engineer*, 221 (1918).

[46] Holm, G. E., Greenbank, G. R., and Deysher, E. F., *Ind. Eng. Chem.*, **19**, 156 (1927).

[47] Greenbank, G. R., and Holm, G. E., *Ind. Eng. Chem. Anal. Ed.*, **2**, 9 (1930).

[48] Horio, M., *Mem. Coll. Eng. Kyoto Imp. Univ.*, **8**, No. 1, 8 (1934); *Chem. Abs.*, **28**, 5339, 7165 (1934).

[49] Nakamura, M., *J. Soc. Chem. Ind. Japan*, **40**, 205B, (1937); *Chem. Abs.*, **31**, 6910 (1937).

The velocities of formation of peroxides during irradiation of tung and castor oils are less than those in linseed and tsubaki oils. The peroxides of all these oils are stable at low temperatures in ultraviolet rays.[50]

In the presence of inert gases, olive, peanut, sesame and colza oils were unaffected by ultraviolet light, but in the presence of oxygen there was an increase in density and a decrease in iodine number. The fluorescence changed from yellow to deep blue as the oils became decolorized.[51]

Olive, linseed and especially cod-liver oil gain in weight on exposure to air in the absence of light, possibly because of the absorption of oxygen. Preliminary irradiation of the oils by ultraviolet light for thirty hours enhances the rate during fifty days up to a limit beyond which it is decreased. In comparison with the others, cod-liver oil behaves as though it had already been irradiated. The formation of a compound with peroxide oxygen (detected by the liberation of iodine from potassium iodide acidified with acetic acid) shows a relation to the time of irradiation similar to that of the increase in weight.[52] Peroxides are formed in olive, mustard, cocoanut, Mahua, castor, sesame and linseed oils, butter and some carbohydrates when air is passed through them during exposure to sunlight. In the absence of air, peroxide formation is decreased. All the oil peroxides have the ability to oxidize slowly a solution of glucose at 40°C.[53] Fats are believed to form ketones by Schmallfuss, Werner and Gehrke[54] and saturated and unsaturated acids, glycerol, some esters, soap, beeswax, and cholesterol act similarly. The higher fatty acids are converted to lower acids, and glycerol yields volatile acids. When methyl laurate or glycerol were used, positive aldehyde tests could be obtained.[55]

Soybean oil is rapidly ketonized by light of wave-lengths under 4100A, several times as rapidly as methyl laurate which is appreciably affected only by rays shorter than 3300A.[56]

The prolonged action of ultraviolet light on lard destroys the material causing luminescence, raises the octoic acid value, and forms the substance responsible for the Kreis reaction of rancid fats.[57] The increase in octoic acid value may be due to pelargonic and azelaic acids formed by oxidation and fission of oleic acid. The substance responsible for luminescence may be a derivative of oleic acid, or of hydroxyoleic acid.

Weak artificial light accelerates the oxidation of beef fat and exposure to direct sunlight for a few minutes suffices to produce rancidity.[58] The reaction is autocatalytic, even brief exposure to light accelerating the subsequent oxidation. In beef fat, bleaching of the lipochrome occurs at a comparatively early stage of the oxidation process. At least during the early stages, oxidation in the presence of

[50] Nakamura, M., *J. Soc. Chem. Ind. Japan*, **40**, 229, 230 (1937); *Chem. Abs.*, **31**, 7682 (1937).

[51] Francesconi, L., and Pinoncelli, L., *Ann. chim. applicata*, **24**, 242 (1934); *Chem. Abs.*, **28**, 6006 (1934).

[52] Delore, P., *Bull. soc. chim. biol.*, **11**, 74 (1929); *Compt. rend. soc. biol.*, **99**, 807 (1928); *Chem. Abs.*, **23**, 724 (1929). See also Zinov'ev, A. A., and Drucker, S. V., *Masloboĭno Zhirovoe Delo*, **13**, No. 2, 6 (1937); *Chem. Abs.*, **31**, 7682 (1937).

[53] Chacrabarti, S. N., and Dhar, N. R., *Indian J. Med. Research*, **17**, 430 (1929); *Chem. Abs.*, **24**, 2166 (1930).

[54] Schmallfuss, H., Werner, H., and Gehrke, A., *Fettchem. Umschau*, **40**, 102 (1933); *Chem. Abs.*, **27**, 3838 (1933).

[55] Schmallfuss, H., Werner, H., and Gehrke, A., *Margarine-Ind.*, **27**, 79 (1934); *Brit. Chem. Abs.* **B**, 846 (1936); Lampitt, L. H., and Sylvester, N. D., *Biochem. J.*, **30**, 2237 (1936); *Chem. Abs.*, **31**, 3311 (1937). For a review, see Schmallfuss, H., Werner, H., and Gehrke, A., *Fette u.-Seifen.*, **43**, 211, 243 (1936).

[56] Werner, H., Gehrke, A., and Minkowski, R., *Margarine-Ind.*, **27**, 93 (1934); *Chem. Abs.*, **29**, 7103 (1935).

[57] Grossfeld, J., *Z. Unters. Lebensm.*, **55**, 376 (1928); *Brit. Chem. Abs.*, **1928B**, 824.

[58] Lea, C. H., *Proc. Roy. Soc.*, **B108** 175 (1931).

light has but little effect on the acidity of the fat. There is a distinct parallelism between the intensity of the Kreis reaction (a pink color test with phloroglucinol and hydrochloric acid in a benzene solution) and the active oxygen content of the fat (determined by the liberation of iodine from potassium iodide in acetic acid and chloroform). At low temperatures, however, the content of active oxygen increases more rapidly in a fat than does its ability to respond to the Kreis test. The reverse is true in bright sunlight. The different susceptibilities of various specimens of beef fat to oxidation depends on the chemical nature of the fat itself rather than upon other tissue constituents.

Coe [59] suggests that under the photosensitizing action of chlorophyll, atomic hydrogen is liberated. This combines with molecular oxygen to form a loosely bound hydrogen peroxide, which unites with the unsaturated bond of the glyceride and produces the rancid compound. The presence of catalase, therefore, is related to its keeping qualities. Other photosensitizers are assumed to be present in animal fats.

Coe and Leclerc [60] observed that on keeping maize or cottonseed oils in darkness or in green light, high peroxide values may be attained without the usual indications of rancidity being observed. Similar samples exposed to full daylight became rancid in the same period. Those kept in the dark do so on subsequent exposure to light. Lampitt and Sylvester [61] found the Issoglio test useful in measuring the initial changes which take place. It is said to give a quantitative measure of these changes before the stage of positive Kreis tests has been reached. The taste of rancid butter fat produced by irradiation of ether and petroleum ether solutions in the presence and absence of air may be the resultant of two different changes, one due to structural changes in the glycerol portion and the other in the constituent to which the fat owes its original taste. These changes may occur independently.[62] The distinction between rancid and tallow-like odors and tastes has been denied by Horowitz-Vlasova, Kachanova and Tkachev,[63] since both seem associated with the formation of various oxidation products such as hydroxystearic acid and epihydrinaldehyde. Lipolysis does not occur. Exposure of milk to sunlight catalyzes the oxidation of the fat.[64] Light also increases the peroxide number of butterfat.[65]

Effects of Colors of Protective Wrappers. Discrepancies are apparent in the reports on the effects of various colors on the deterioriation of oils. Greenbank and Holm,[66] Lea [67] and Coe [68] found green light to be least and orange light the most active. Blue light was thought to be somewhat more active than red light. Coe believed that oils protected by opaque or green wrappers showed no organoleptic rancidity after seven months, although they gave strong Kreis,

[59] Coe, M. R., *Oil and Soap,* **15,** 230 (1938); *Chem. Abs.,* **32,** 8178 (1932).

[60] Coe, M. R., and Leclerc, J. A., *Ind. Eng. Chem.,* **26,** 245 (1934).

[61] Lampitt, L. H., and Sylvester, N. D., *Chim. et industrie, Special No.* **642** (March, 1931); *Chem. Abs.,* **25,** 3737 (1931).

[62] For a general discussion of the chemistry of rancidity, see Russell, E. E., *Can. Chem. Met.,* **20,** 346 (1931).

[63] Horowitz-Vlasova, L. M., Kachanova, E. E., and Tkachev, A. D., *Z. Untersuch. Lebensm.,* **69,** 409; *Chem. Abs.,* **29,** 7679 (1935).

[64] Barkworth, H., *Dairy Inds.,* **3,** 7 (1938); *Chem. Abs.,* **32,** 2230 (1938).

[65] Ritter, W., and Nussbaumer, T., *Schweiz. Milchztg.,* **64,** 59 (1938); *Chem. Abs.,* **32,** 7148 (1938).

[66] Greenbank, G. R., and Holm, G. E., *Ind. Eng. Chem.,* **25,** 167 (1933).

[67] Lea, C. H., *J. Soc. Chem. Ind.,* **52,** 146T (1933).

[68] Coe, M. R., *Siebel Tech. Rev.,* **9,** No. 2, 51 (1934); *Science,* **75,** 585 (1932); *Ind. Eng. Chem.,* **26,** 245 (1935); Coe, M. R., and Leclerc, J. A., *Cereal Chem.,* **9,** 519 (1932); *Chem. Abs.,* **26,** 6030 (1932); *Cereal Chem.,* **11,** 241 (1934); *Chem. Abs.,* **28,** 4925 (1934); *Oil and Soap,* **11,** 189 (1934); *Brit. Chem. Abs.,* **B,** 1018 (1934); *Oil and Soap,* **12,** 231 (1935); *Chem. Abs.,* **29,** 8371 (1935); *Oil and Soap,* **13,** 197 (1936); *Chem. Abs.,* **30,** 6587; *Oil and Soap,* **14,** 171 (1937); *Chem. Abs.,* **31,** 6494 (1937).

peroxide and von Fellenberg tests. Davies, however, believed [69] that the preservative effect of Cellophane wrappers depends more upon the depth of color than upon the actual color. Deep green, blue, red or dark brown were equally effective in preventing the autoxidation of the fat of biscuit meal in exposures of forty hours to sunlight. Light green and heliotrope wrappers allowed some oxidation to occur and lightly tinted papers were entirely ineffective. Thin vegetable parchment did not allow active rays to pass, greaseproof paper allowed some to penetrate and transparent paper had no retarding action.

Morgan [70] attacked the conclusions of Greenbank and Holm and of Coe. He finds in studies on potato chips that yellow or red light has little ability to cause rancidity, the deleterious action being due chiefly to blue and ultraviolet light. He did not rely, as others had done, upon oxygen uptake or the peroxide test, but determined the time of exposure required for rancidity to become evident to odor and taste. The ratio of this to the time required for the same effects to be

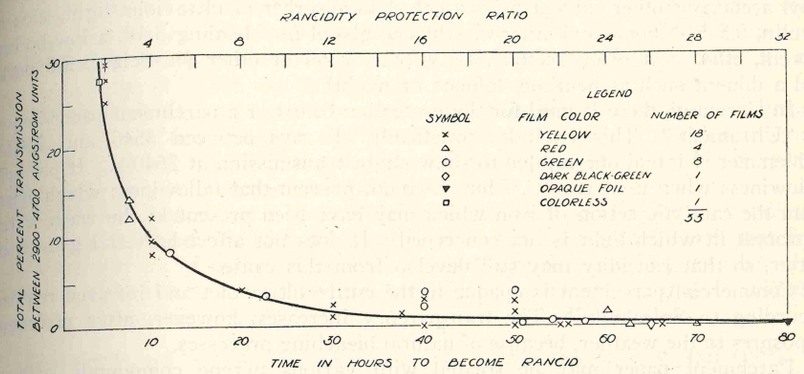


FIGURE 120. Rate of Rancidity Development in Potato Chips as Affected by Total Percentage Transmission of Light Wave-lengths 2900 to 4700A (Morgan, *Industrial and Engineering Chemistry*).

produced in the same lot of chips simultaneously exposed in uncolored transparent cellulose gave the rancidity-retarding value of the film. Both daylight and a General Electric S-2 sunlamp were used as sources. It was believed that the rancid odor and taste are due to aldehydes of high molecular weight formed by the oxidation of unsaturated linkages. Tests of several hundred colored transparent cellulose wrappers indicated that their utility in retarding rancidity depended upon their transmission of blue and ultraviolet light. (See Figure 120.) Very small amounts of ultraviolet light had an extremely disproportionate effect. The results of the earlier observers were ascribed to their failure to take into account the passage of small amounts of ultraviolet light through some of their wrappers. The visible color tells nothing regarding the effectiveness of a wrapper. Morgan developed a yellow transparent sheeting of cellulose, known as Sylphrap RR Old Gold [71] (from Sylvania Corporation) of high visible transparency and complete ultraviolet opaqueness in the usual 0.001-inch thickness. The only visible light cut

[69] Davies, W. L., *J. Soc. Chem. Ind.,* **53,** 148T (1934).

[70] Morgan, W. L., *Ind. Eng. Chem.,* **27,** 1287 (1935).

[71] Morgan, W. L., *Modern Packaging,* May, 41, November, 84 (1934).

off is blue and practically all articles and foodstuffs wrapped in it appear in approximately normal color shades of red, brown, yellow or green. It is also recommended for protecting flavors of fruit juices, wines, brandies, flavoring extracts and perfumes as well as such drugs as phenol, calomel, quinine sulfate, and chloramine-T. It also retards the yellowing of paper and the sunlight aging of rubber.[72]

Wickmann [73] employs a deposit of particles of metal of atomic dimensions on the surface of gelatin or cellulose sheets in a granular non-flaking and non-cracking layer, giving the appearance of a continuous, lustrous coating.

As absorbing agents, Hunter proposes,[74] for incorporation in cellulosic wrapping paper, diaminobenzophenone and its homologs, derivatives of phenylhydrazine and aliphatic keto-acids, aminonaphthalenesulfonic or trisulfonic acids, *p*-hydroxyazobenzene, diphenylaminobenzene, resorcinolazobenzene or cresolbenzene. These absorb over the range 3200 to 4000A, and particularly 3500 to 3700A. Grant [75] employs on regenerated cellulose wrappers a coating composition of pyroxylin 3, amyl acetate or other solvent 5-25, a colorless absorber of ultraviolet light, such as esculin, 0.5-5.0, monoethyl ether of ethylene glycol for blending 3-10, a low-boiling solvent, ethyl acetate or acetone, 11-30, castor oil or other plasticizer, 2-5 parts, and a diluent such as benzene, toluene or naphtha.

In Germany, there is used for the protection of butter a parchment paper known as "Ultrament." This excludes practically all rays between 3540 and 2000A. Schlemmer [76] found one sample to show slight transmission at 2640A. It prevents tallowiness when used at 5°C.[77] but it cannot prevent that tallowiness which arises from the catalytic action of iron which may have been present in the wash water, a process in which light is not concerned. It does not affect bacterial growth on butter, so that rancidity may still develop from this cause.

Commercial parchment is opaque in the entire ultraviolet and infrared regions, according to Solechnik.[78] The transparency increases, however, after prolonged exposures to the weather, because of natural bleaching processes.

Parchment paper may be treated with various pyrene compounds such as sodium 3,5,8,10-pyrene tetrasulfonate, sodium 3-benzoyl-aminopyrene-*p*-disulfonate and the urea of sodium 4′-aminobenzoyl-3-aminopyrene disulfonate.[79] In other filters, one part of 3,5-dimethoxypyrene is dissolved in 99 parts of nitrocellulose lacquer and the solvent evaporated to leave a colorless film insoluble in water. A film of cellulose hydrate may also be passed through a bath containing 1 per cent

[72] Morgan, W. L., U. S. P. 2,043,860, June 9, 1936; *Chem. Abs.*, **30,** 5442 (1936); British P. 453,438, Sept. 8, 1936; *Chem. Abs.*, **31,** 1113 (1937). Dyes are used incorporated in regenerated cellulose sheets. Joseph, C., U. S. P. 2,038,114, April 21, 1936; *Chem. Abs.*, **30,** 3913 (1936); British P. 410,170, May 10, 1934; *Chem. Abs.*, **28,** 6312 (1934) uses as the absorbing agent a nonglucosidic coumarin derivative such as umbelliferone-acetic acid. Esculin, quinine, salol and anthracenes are also suggested. All patents to Sylvania Industrial Corp.

[73] Wickmann, P. A., U. S. P. 2,039,372, May 5, 1936, to Sylvania Industrial Corp.; *Chem. Abs.*, **30,** 4232 (1936).

[74] Hunter, A. S., French P. 791,492, Dec. 11, 1935, to Soc. des usines chimiques Rhône-Poulenc; *Chem. Abs.*, **30,** 4232 (1936); Hunter, A. S., U. S. P. 2,062,179, Nov. 24, 1936, to E. I. du Pont de Nemours & Co.; *Chem. Abs.*, **31,** 789 (1937); Hunter, A. S., U. S. P. 2,129,131-2, Sept. 6, 1938, to E. I. du Pont de Nemours & Co.; *Chem. Abs.*, **32,** 8618 (1938).

[75] Grant, D. H., U. S. P. 2,058,786, to Stanco, Inc.; *Chem. Abs.*, **31,** 187 (1937).

[76] Schlemmer, F., *D. Molkerei-Ztg.*, **56,** 185 (1935); *Chem. Abs.*, **29,** 2611 (1935); for a detailed discussion of factors affecting the deterioration of butter, see Jensen, J., and Ritter, W., *Lait*, **18,** 758 (1938); *Chem. Abs.*, **32,** 7147 (1938).

[77] Maier, Fr., *Deut. Molkerei-Ztg.*, **55,** 1477 (1934); *Chem. Abs.*, **29,** 2611 (1935).

[78] Solechnik, N. Y., *Bumazhnaya Prom.*, **13,** No. 8, 24 (1934); *Chem. Abs.*, **29,** 1244 (1935). See also Sommer, H., and Becker, J., *Zellstoff u. Papier*, **13,** 335 (1933); *Chem. Abs.*, **27,** 4669 (1933).

[79] British P. 457,708, Nov. 30, 1936, to I. G. Farbenind. A.-G.; French P. 804,582, Oct. 27, 1936; *Chem. Abs.*, **31,** 3602 (1937); see also Eggert, J., and Wendt, B., German P. 640,908, Jan. 15, 1937, who use a urea derivative of sodium *p*-aminobenzoyl-*p*-phenylenediamine sulfate; *Chem. Abs.*, **31,** 5484 (1937).

of the urea of sodium 4′-aminobenzoyl-3-aminopyrene-disulfonate at 50°C. so that every part of the foil is covered by the liquid for one minute.

Gerngross and Callo [80] use a dilute aqueous solution of pine-bark or quebracho extract in treating transparent papers or films of cellulose derivatives to make them impermeable to ultraviolet rays.

Paper milk bottles protect skim milk, whole milk or buttermilk against the action of sunlight in causing burnt flavors, but they do not protect whole milk or cream or homogenized whole milk and cream against tallowy flavors.[81] The burnt flavor predominates in low-fat and the tallowy flavor in high-fat products. Both commonly occur together in whole milk exposed to the sun. Homogenization of milk and cream accelerates the development of tallow flavor in sunlight, but retards that due to copper catalysis. The burnt flavor may have its source in the protein-free serum. It seems to be related to the fading of lactoflavin, which is the primary cause of the bleaching of milk in sunlight. This bleaching does not occur in paper bottles.

Ried [82] believed the stability of milk could be improved by keeping it in metal cans which had been previously irradiated by ultraviolet rays. He also proposed to pack butter and cheese in irradiated metal foil and believed the growth of yeast could be influenced by the use of irradiated metal vessels.

Soap bars with traces of iron or copper oxide darken in four days in diffused daylight and in a few hours in sunlight or ultraviolet light.[83] Sudden irregular after-darkening and rancidity of soap bars is traced to small quantities of rust or copper oxide from corroded parts of the equipment.

It has been claimed that a bactericidal substance may be obtained by irradiating a non-saponifiable portion of fatty material until it has an activity such that from 2 to 7 mg. per cc. of maize oil is fatal to yeast. Such a product may be mixed with inert oils or with lanolin to form medicinal preparations or may be added to cosmetics or shaving soaps.[84]

[80] Gerngross, O., and Callo, A., British P. 459,335, Jan. 6, 1937; *Chem. Abs.*, **31,** 4021 (1937).

[81] Doan, F. J., and Myers, C. H., *Milk Dealer*, **26,** No. 1, 76 (1936); *Chem. Abs.*, **31,** 2304 (1937).

[82] Ried, O., Austrian P. 121,243, Sept. 15, 1930; *Chem. Abs.*, **25,** 2367 (1931).

[83] Wittka, F., *Seifensieder-Ztg.*, **54,** 740 (1927); *Chem. Abs.*, **22,** 177 (1928).

[84] British P. 423,354, Jan. 22, 1935, to Standard Brands; *Chem. Abs.*, **29,** 4526 (1935).

Chapter 30

Processes Involving the Polymerization of Oils, Paints and Varnishes

In discussing the bleaching of oils, it was impossible to avoid mention of the polymerization of unsaturated oils. The commercial processes which depend largely upon polymerizing and oxidizing effects are complex and are not as yet thoroughly understood. In addition, in unsaturated oils there are stereoisomeric transformations at double bonds. A separate treatment of these, and possibly other photochemical changes is scarcely possible as yet in a discussion of the mechanism of the drying of oils as influenced by light. Color changes also occur during drying.

Tung oil is the most suitable oil for studying the drying process because of its comparative freedom from mixed glycerides and because of its ability to yield purifiable products.[1] It was pointed out by Marcusson[2] that the white mass of melting point 32°C. formed in chinawood oil by ultraviolet light in the absence of oxygen cannot be a simple product of polymerization since the fatty acids liberated from it differ from those liberated from the original oil in melting at 71°C. They consist chiefly of β-eleostearic acid, an isomer of the α-form present in the original oil. Tung oil has 90 per cent of α-eleostearic (eleomargaric) acid. Accordingly, the formation of β-eleostearic acid is similar to the type of change discussed previously in connection with cinnamic acid. The formation of β-eleostearin causes the film of dried tung oil to lack durability. In addition to this process, there occurs also the formation of a small amount of an infusible polymerization product of β-eleostearin. This also is analogous to the type of change occurring in the cinnamic acid series. The change may be completed by 48 hours of irradiation, according to Böeseken and Ravenswaay.[3]

Manecke and Volbert noted[4] that eleostearic acid and its methyl ester have a deep absorption band at 2650 to 2750A. Dingwall and Thomson[5] went further in showing that two forms can be definitely identified by absorption curves. By studying the absorption spectrum of the α-form in alcoholic solution after various periods of mercury arc irradiation, it was found that during the first two minutes it tended to pass over into the β-form. Continued irradiation, however, caused profound changes. When a 15-per cent solution of the α-acid in 90-per cent alcohol was irradiated for two hours it was converted into an acid that had the same absorption spectrum (2500 to 2850A) as the acid obtained from the solid glyceride. The absorption curves obtained by Manecke and Volbert for linoleic acid and its ester were different. They resembled those of oleic and crotonic acids with a slight increase in the intensity of absorption and a displacement of the characteristic weak absorption bands in the direction of longer wave-lengths. Absorption curves for acetic, elaidic, linoleic, eleostearic and stearoleic acids have recently been given by van der Hulst.[6] It will be recalled that in discussing the absorption of various unsaturated open-chain compounds, Smakula had shown the absorption to increase with the number of conjugated double bonds.

Eleostearic acid in carbon tetrachloride adds bromine rapidly in the light of a Uviol lamp until three double bonds are saturated.[7]

Eighteen grams of α-eleostearic acid in 180 gms. of petroleum ether in a freezing mixture was exposed by Bauer and Rohrback[8] in a quartz flask to ultraviolet light while adding bromine dropwise to the extent of six atoms per molecule. A white solid which separated after several hours, during which there was much evolution of hydrogen bromide, had the formula $C_{18}H_{30}O_2Br_6$. On debromination with zinc in alcohol, it gave β-eleostearic acid. An oily by-product of the hexabromide had a bromine content between that of penta- and hexa-bromide. When debrominated, it gave an oil with a bromine content between di- and tri-bromoeleostearic acid.[9] Of the three (conjugated) double bonds usually only two add bromine unless the solution is exposed to ultraviolet rays.[10]

Ellis found that chinawood oil at six inches from a mercury arc became so brittle after an hour that it could easily be pulverized to a white powder of iodine value 93. Linseed oil gave a resilient translucent jelly of practically the same color as the original oil.

Working with thin films of tung oil on glass slides, Eibner and Rossmann[11] found that exposure to sunlight or for ten minutes to a mercury arc causes a rapid formation of the crystalline β-eleostearin. Although at room temperatures, this is soluble in the unchanged oil, precipitation occurred if the film was kept at 0°C. The crystals could be observed microscopically under polarized light. This transformation is regarded as the first step in drying. In the absence of light, this isomerization did not occur. Oxygen is essential to the change of pure β-eleostearic acid to the amorphous condition, "filming"; this autoxidation is favored by light and by increase of temperature. The observation that during the conversion of this material into a film from 7 to 10 per cent of oxygen is absorbed invalidated the older theory that drying or film formation was a pure polymerization process. Examination of the fatty acids recovered from the product also showed that considerable oxidation had occurred. Polymerization probably also occurs so that film formation is a mixed process, "autoxypolymerization." Thus, if a tung oil containing β-eleostearin be exposed in a thin film, oxygen is primarily absorbed by the dissolved β-glyceride in the surface layers; the autoxypolymerization products are at first colloidally dispersed and then, by rapid transition to the gel condition, constitute a first disperse phase leading to film formation. Comparative experiments on the behavior of thin and thick films showed that the absorption of oxygen continues up to the drying point, and constitutes a principal reaction. Not all of the original α-eleostearin is transformed to the β-form before the autoxypolymerization occurs, for a tung oil kept in darkness for three to four weeks dried to a clear film. The greater part is directly autoxidized to a film.

[1] A critical review of the earlier work on the drying of oils and the nature of the "oxyn acids" was given by Eibner, A., and Munzert, H., *Chem. Umschau*, **34**, 89, 101 (1927); *Brit. Chem. Abs.*, 417 (1927); *Chem. Abs.*, **21**, 2071 (1927). See also Morrel, R. S., *Chemistry and Industry*, **56**, 795 (1937).

[2] Marcusson, J., *Z. angew. Chem.*, **35**, 543 (1922); *Z. deut. Oel-Fett Ind.*, **43**, 162 (1923).

[3] Böeseken, J., and Ravenswaay, H. J., *Rec. trav. chim.*, **44**, 241 (1925). Eibner, A., Merz, O., and Munzert, H., *Chem. Umschau*, **31**, 69 (1924); Nonaka, M., *J. Chem. Ind. Japan*, **24**, 1272 (1921); Morrell, R. S., *J. Chem. Soc.*, **101**, 2082 (1912). Blom, A. V., attributes the change to rays of long wave-length, *Chem. Umschau, Fette Oele Wachse Harze*, **36**, 229 (1929); *Chem. Abs.*, **23**, 6336 (1929).

[4] Manecke, W., and Volbert, F., *Farben-Ztg.*, **32**, 2829, 2887 (1927); *Brit. Chem. Abs.*, **B**, 821 (1927).

[5] Dingwall, A., and Thomson, J. C., *J. Am. Chem. Soc.*, **56**, 899 (1934).

[6] van der Hulst, L. J. N., *Rec. trav. chim.*, **54**, 639 (1935).

[7] Kaufmann, H. P., and Luten-Berg, K., *Ber.*, **62B**, 392 (1929). In methyl alcohol, two of the double bonds are saturated in darkness within an hour but the third only begins to react after fifteen hours. *Ber.*, **59B**, 1390 (1926).

[8] Bauer, K. H., and Rohrback, E., *Chem. Umschau Fette, Waxe, Harze*, **35**, 53 (1928); *Chem. Abs.*, **22**, 2073 (1928).

[9] See also Kaufmann, H. P., *Ber.*, **59**, 1395 (1926); Böeseken, J., *Rec. trav. chim.*, **46**, 619 (1927).

[10] Kaufmann, H. P., and Baltes, J., *Ber.*, **69B**, 2670 (1936); *Chem. Abs.*, **31**, 2032 (1937).

[11] Eibner, A., and Rossmann, E., *Chem. Umschau*, **35**, 241 (1928); *Chem. Abs.*, **23**, 291 (1929); *Brit. Chem. Abs.* **B**, 934 (1928). See also Merz, O., *Farbe und Lack*, **31**, 332, 343 (1926); *Chem. Abs.*, **21**, 184 (1927).

Microscopic examination of films of chinawood oil on glass revealed a shrinkage in volume and the formation of fine cracks while the film was still moist, the cracks reaching through to the bottom.[12] This contraction coincides with the formation of β-eleostearin from the α-form. The next step in drying is the formation of folds at right angles to the cracks, increasing the volume and frequently pushing the cracks together again to form a double-lipped joint; this folding coincides with the absorption of oxygen by the α-eleostearin. Certain observations, however, stand in opposition to this simple theory. β-Eleostearin alone, when melted, will show contraction and crack formation and, as previously stated, the β-form also dries by a primary oxidation followed by polymerization. Light seems essential to the wrinkling, since clear, non-wrinkled films are obtained by drying the oil in darkness. In the light of the quartz lamp, this oil never dries clear; in sunlight at lower temperatures, there is wrinkling without cracking. α-Eleostearin does not appear to cause cracking at room temperature. It has also been observed in a black wood oil varnish that a network of fine cracks can form after the wrinkles have appeared, passing through the latter at all angles. Rossmann[13] states also that when ionized oxygen (produced by a flame, ultraviolet light or radioactive materials) was present during the drying of tung oil, wrinkles were formed, but that wrinkles did not form in the presence of ionized nitrogen or illuminating gas.

It has recently been suggested that a third form of eleostearic acid may exist. This is the punicic acid obtainable also from the seeds of the pomegranate. Ultraviolet light converts it into β-eleostearic acid.[14]

The properties of so-called "light-struck" tung oils were studied by Gardner and Parks.[15] Upon heating, the oils were quickly transformed into a clear liquid condition and could then be used for the production of varnishes as satisfactory as those made from oils which had not been "light-struck." Oils which had been exposed to sunlight for about six months could be brought back to a normal state by heating to about 60°C., although then their solidification points were very much lower than those of normal oils. Warming samples of the exposed oils with an equal volume of acetone gave clear transparent solutions, but on standing overnight these solutions gave heavy deposits of white crystals. Eibner would doubtless consider these as β-eleostearin.

Rossmann[16] exposed the α- and β-forms of eleostearic acid with and without solvents to sunlight and to the light of the quartz mercury arc. The products yellowed more or less, the iodine number decreased and the molecular weight increased. The decrease in iodine number determined by the usual methods did not indicate a loss of more than one double bond, but by the use of special methods it appeared to decrease by two in some cases. Various types of dimolecules may form through the loss of a double bond of each. It is also possible that the 1- and 6-carbon atoms of the three conjugated groups may join forming ring complexes. The amount of polymerization which occurs in 144 hours under the Hanau quartz lamp could be attained in a few minutes by heating at 300°C.

Lévy[17] has also described the microscopic wrinkling and folding of the frosty surface of tung oil films dried in air and light. The films formed by the much slower drying of the oil in darkness (six to eight weeks) are, if thin, nearly or

[12] Eibner, A., and Rossmann, E., *Chem. Umschau,* **35,** 281 (1928); *Chem. Abs.,* **23,** 1516 (1929).
[13] Rossmann, E., *Farben-Ztg.,* **38,** 1288 (1933); *Chem. Abs.,* **27,** 5557 (1933).
[14] Farmer, E. H., and van den Heuvel, F. A., *J. Chem. Soc.,* 1809 (1936).
[15] Gardner, H. A., and Parks, H. C., *Circular No.* **256,** *Paint Manufacturers Association,* December, 1925.
[16] Rossmann, E., *Fettchem. Umschau,* **40,** 96 (1933); *Chem. Abs.,* **27,** 5057 (1933).
[17] Lévy, P., *Recherches et inventions,* **14,** 340 (1933); *Chem. Abs.,* **28,** 3918 (1934).

completely free from frostiness. When dried in light, but in the dry atmosphere of a sulfuric acid desiccator, three weeks are required and only the thin films exhibit frostiness. Drying in a dry or moist vacuum requires about a year, but the surface is smooth. There is a loss of 1 to 3 per cent in weight. On opening the tubes there is an ethereal odor. Pressed oils do not solidify even when exposed for several months to sunlight or to an electric filament lamp. Oil obtained by extraction with petroleum ether solidifies in from a few days to a year in darkness, in a few days to a month in sunlight and in a few hours in the light of a mercury arc lamp. X-ray diffraction diagrams indicate that the solidified oil has a crystalline structure. In studies by means of the Siedentopf cardioid ultramicroscope, McCloskey and France[18] demonstrated a considerable increase in the number of colloidal particles and in the viscosity of tung and non-acidified linseed oils on irradiation.

Linseed Oil. The drying of linseed oil has been the subject of many investigations but cannot be said to be as well understood as is that of tung oil.[19] Kaufmann[20] gave data on the effects of light on the rate of the bromination of linseed oil in carbon tetrachloride and in methyl alcohol saturated with sodium bromide. The results, in Table 23 cited by Knauss and Smull,[21] are given as the equivalent of iodine absorbed by equal amounts of oil.

Table 23.—Bromination of Linseed Oil (Iodine No. 182)

	CCl_4		CH_3OH and NaBr	
Time	Dark	Sunlight	Dark	Sunlight
2 minutes	152.0	178.1	....	....
10 "	151.2	183.0	156.2	161.3
30 "	152.8	190.5	157.4	163.8
60 "	156.8	194.3	160.7	164.3
24 hours	183.0	239.5*	183.3	182.0
48 "	182.0	252.0	183.5	181.6

* No mention is made by Kaufmann as to whether any substitution had taken place to give these high values.

Knauss and Smull determined the rates of substitution and addition when bromine was kept with the fatty acids from poppyseed oil, soybean oil, linseed oil and perilla oil for one hour in darkness. They then observed increases in these values during subsequent exposure in quartz tubes to ultraviolet light during an hour. Similar observations were made upon oleic, linoleic and linolenic acids. The mixed fatty acids of the different oils all absorbed more bromine when irradiated than in darkness. This was held to indicate the presence of stereoisomers formed by light and not determinable by the usual methods of analysis. The possibility of a direct action of light upon the bromine does not seem to have been considered, probably because this effect would have been expected by visible rather than ultraviolet light.

Goldschmidt and Freudenberg[22] found that ultraviolet light failed to cause the polymerization of linolenic acid and its esters *in vacuo,* the process occurring only through oxygen bonds. Genthe[23] made early studies of the use of ultraviolet rays in the drying of linseed oil. It was exposed on filter paper to an atmosphere of oxygen in a quartz flask. During the first two hours of irradiation the absorption

[18] McCloskey, K. E., and France, W. G., *Ind. Eng. Chem.,* **27,** 160 (1935).
[19] For a review of early work, see *Farbe und Lack,* 629 (1926).
[20] Kaufmann, H. P., *Z. Untersuch. Lebensm.,* **51,** 3 (1926); *Ber.,* **59,** 1390 (1926).
[21] Knauss, C. A., and Smull, J. G., *J. Am. Chem. Soc.,* **49,** 2808 (1927).
[22] Goldschmidt, S., and Freudenberg, K., *Ber.,* **67B,** 1589 (1934).
[23] Genthe, A., *Z. angew. Chem.,* 2090 (1906).

of oxygen was slight. In the third hour, it became very rapid, gradually diminishing in rate during subsequent hours. No formation of ozone was noted.

In the laboratory of the senior author, samples of linseed oil were found to be considerably bleached by ultraviolet light [24] and in the case of the raw oil, practically no skin was formed over the top. With boiled oil, a film was formed in six hours if there was free access of air. In one case in which the oil was exposed in a thin layer over water, the oil became turbid and apparently a very stable emulsion was formed. In another case a sample of raw oil was exposed

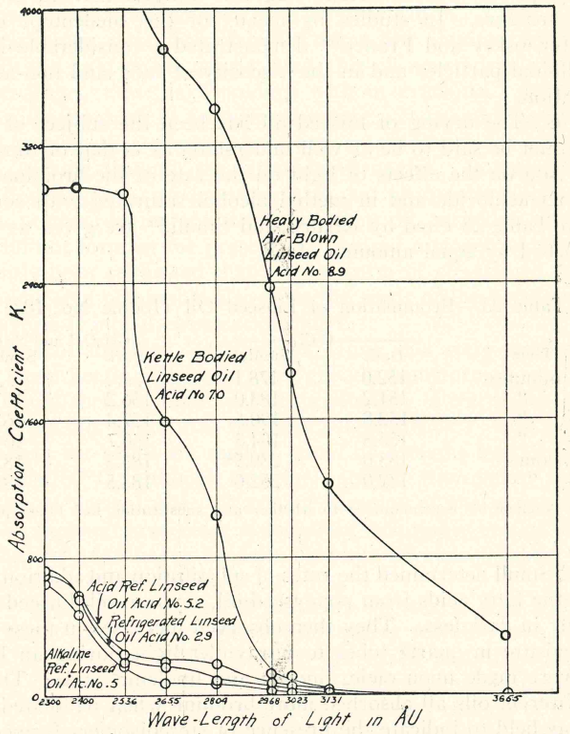


FIGURE 121. Absorption Shown by Several Samples of Commercial Linseed Oils (Stutz, *Industrial and Engineering Chemistry*).

for seven hours in a closed chamber in an atmosphere of steam. The oil, which had been quite dark at the beginning, was bleached to a light straw color.[25]

Stutz[26] found the irradiation of raw linseed oil by ultraviolet in the presence of nitrogen to cause a marked decrease in the iodine number. This was confirmed by Knauss and Smull, who found that a sample of raw oil with iodine number of 180 showed only 148 after exposure for eighteen hours in dry carbon dioxide. But when this sample of oil was brominated in ultraviolet light for thirty minutes, the total bromine absorbed was equivalent to an iodine number of 190. In the

[24] See also Würth, K., *Farben Ztg.*, **33**, 1852 (1928); *Chem. Abs.*, **22**, 4261 (1928).
[25] Ellis, C., and Wells, A. A., *Chem. Eng.*, 116 (1918).
[26] Stutz, G. F. A., *Ind. Eng. Chem.*, **18**, 1238 (1926).

first exposure of the raw oil in the presence of carbon dioxide, the ultraviolet rays caused a mutation of the stable isomers to labile forms. In the second exposure in which bromine was used, the action of the radiation stimulated the addition of halogen to the isomers formed in the first irradiation. It is known that labile isomers react very slowly with halogen and easily with oxygen. This too was found to be the case, for the oil from the first exposure (iodine number only 148) dried more rapidly than the raw, unexposed oil. It is apparent, therefore, that the

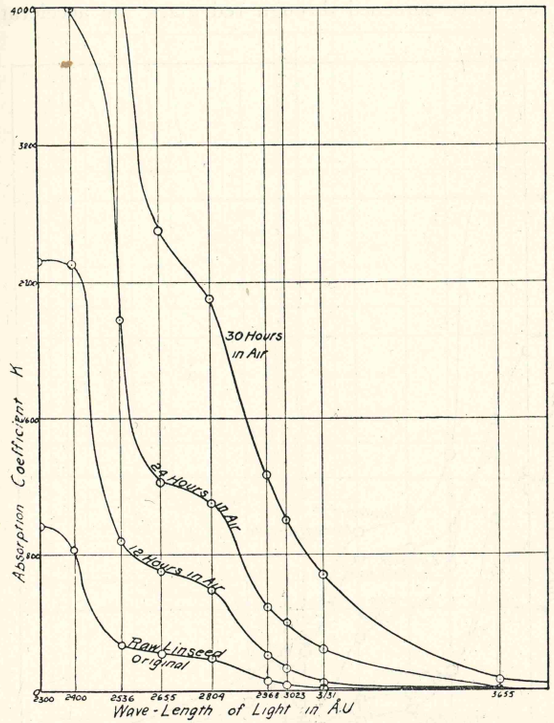


FIGURE 122. Change in Absorption Spectrum Shown by Raw Linseed Oil after Exposure to Ultraviolet Light in the Presence of Air (Stutz, *Industrial and Engineering Chemistry*).

ultraviolet rays must have simply stimulated the halogenation. It is unlikely that they could in thirty minutes have changed the labile form to the stable form.

An apparatus for oxidizing oils is described by Schofield.[27] The oil, such as linseed oil, is sprayed through a chamber illuminated by a high-tension electrical discharge. Purified and dried air is also supplied to the chamber, under pressure and at a temperature of about 250°C.

Gardner and Parks [28] found direct sunlight to accelerate the drying of a film of raw, unsiccatized linseed oil exposed to the air. There were no differences in the drying times in direct sunlight or in sunlight filtered through plain, ground,

[27] Schofield, H., British P. 227,212, Oct. 16, 1923; *J. Soc. Chem. Ind.*, 180 (1925).
[28] Gardner, H. A., and Parks, H. C., *Circular* 172, *U. S. Paint Manuf. Assoc.*, March, 1923.

red, amber, blue or green glass. When, however, diffused daylight was employed the following times of drying were noted: Pure unfiltered light, 4 days; amber glass, 11 days; blue glass, 13 days; darkness, plain glass, ground glass, red glass or green glass, 14 days. The effect of heavily siccatizing the oil was to cause the films under all conditions, including exposure in darkness, to dry in six hours. Previous exposure of a film of raw unsiccatized linseed oil to the ultraviolet rays of an iron arc for thirty minutes produced a great acceleration in drying, which was shown to be independent of the heat resulting from the irradiation. When the ultraviolet rays were screened through red glass, the accelerating effect was lost.

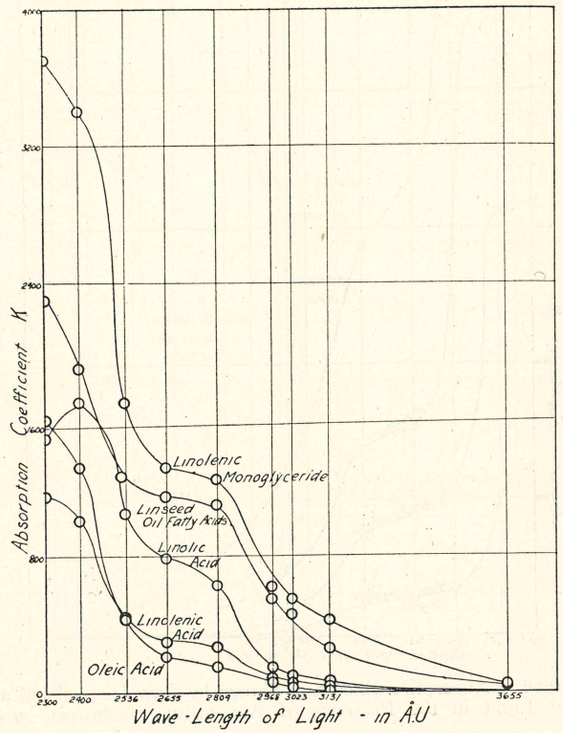


FIGURE 123. Absorption Shown by Acids Contained in Linseed Oil and Monoglyceride of Linolenic Acid (Stutz, *Industrial and Engineering Chemistry*).

Stutz [29] studied the influence of ultraviolet rays on a number of paint oils at 50°C., comparing their physical properties at various intervals. He also measured the absorption of the rays by these oils. In general, it increases with the molecular weight and body. The effect of exposure on wet oils is similar to the effect of heat and air-blowing. A boiled linseed oil absorbs the light almost completely at the surface. A raw oil, however, allows the light to penetrate a considerable distance. (Fig. 121 gives the absorption of several commercial samples.) Oils dried by exposure to ultraviolet light usually have a lesser absorption than those

[29] Stutz, G. F. A., *Ind. Eng. Chem.*, **18**, 1235 (1926); **19**, 897 (1927).

dried in diffused daylight. (See Fig. 122.) Practically all the oils studied, including linseed, tung, soybean, poppyseed and perilla oils, have high absorption of wave-lengths shorter than those at the limit of the sun's spectrum. Because the absorption is so nearly complete near the surface, changes occur there only and the properties of the underlying film are less affected. The radiations of sunlight, however, can penetrate more deeply. This difference deserves consideration in interpreting the results of accelerated weathering tests discussed in a subsequent section. The longer the oil is exposed the more it absorbs and, therefore,

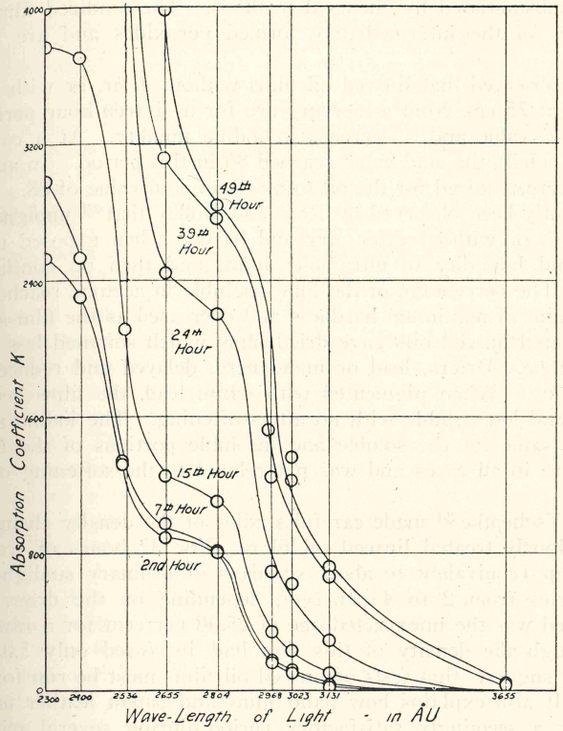


FIGURE 124. Absorption Shown by Several Samples of Linseed Oil Taken at Intervals during an Air-Blow (Commercial Scale) (Stutz, *Industrial and Engineering Chemistry*).

the greater the effect of light, which is cumulative. Bodying the oil seems merely to increase its content of absorbing materials. It cannot be due to an increase in acid content since the pure acids themselves have a lower absorption (see Fig. 123) than oil samples containing only 4 or 5 per cent of such acids. The similarity between the effects of ultraviolet on oil and the absorption changes during an air-blow of linseed oil (Fig. 124) make it probable that the decomposition or weathering of an oil film is simply a continuation of the drying of the film, the same reaction or reactions being involved in both.[30]

[30] See also Becker, J., and Brückersteinkuhl, K., *Z. Kinderheilk.*, **43**, 566 (1927). For some observations on the effects of light on sunflower oil, see Kozin, N. I., and Fridlyanskaya, F. M., *Masloboino Zhirovoe Delo*, **12**, 529 (1936); *Chem. Abs.*, **31**, 5191 (1937).

Eibner and Munzert [31] noted that a linseed oil film in direct sunlight can lose in weight (after a first sharp increase due to oxidation) and may resoften, so that the standard test should be made in diffused daylight. Two oils treated with ultraviolet light were found to have gelatinized throughout their bodies after standing in darkness for several months, their acetyl numbers rising from the original 1.5 and 2.8 to 60.7 and 71.39, respectively, and their hexabromide numbers dropping from the original 51.5 to 13.8 and 9.6, respectively. Their gasoline-insoluble hydroxy-acids had increased from zero to 42.8. The normally dried films of linseed and poppyseed oils were thought to consist of glycerides of oxy-acids, although this could not be substantiated by chemical methods. The oxidized films are condensation products of the intermediately formed peroxides and are not true oxyglycerides.

Marling [32] observed that linseed oil films without drier, or with a cobalt drier, on irradiation at 75 cm. from a mercury arc for a sixteen-hour period showed an increase in acid value and a decrease in iodine number. At a concentration of 0.015 per cent cobalt, the acid value reached 86 in this period. In an indoor aging test, 84 days were required for the oil to reach an acid value of 88.

It has recently been observed by Rose and Bolley that [33] unpigmented films of linseed oil, with or without drier, dry and harden when exposed under constant temperature and humidity to ultraviolet light, and then on continued exposure soften again. The percentage of the film insoluble in acetone reached a maximum at about the point of maximum hardness and decreased as the film softened again. The less saturated linseed oils gave dried films which softened less and were less soluble in acetone. Driers, lead or manganese, delayed and reduced the amount of after-softening. When pigmented with white lead, the films became progressively harder and less soluble with no after-softening. The iodine number, which was about the same for the soluble and insoluble portions of the film, decreased during exposure in all cases and was not related to the softening or solubility of the films.

Clark and Tschentke [34] made careful studies of the density changes during the drying of variously treated linseed oil films. For 32 hours of treatment by an intense sunlamp (equivalent to about six days of ordinary sunlight) the change in density varies from 2 to 4 per cent, depending on the drier. The highest change recorded was the unexpected one of 25.06 per cent for a raw oil film aged 226 days, though the density of this film had increased only 5.03 per cent in 68 days. This suggests that tests of linseed oil films must be run for a sufficiently long period. It also explains how paint films and patent leather may fail rather suddenly after a seemingly satisfactory period during several months. In the presence of driers this increase after periods of 248 days amounts to only 14 or 15 per cent.

Increases in density under ultraviolet light are smaller than in sunning, even though films may assume the same appearance and dryness. Where superposed films are involved, the mechanism of ultraviolet aging differs from that of sunning. After a film has been subjected to sunning or ultraviolet aging and is then placed in darkness, the increase in density continues at an increased rate. This is

[31] Eibner, A., and Munzert, H., *Chem. Umschau Fette, Oele, Waxe und Harze,* **34,** 89, 101 (1927); *Chem. Abs.,* **21,** 2071 (1927).

[32] Marling, P. E., *Ind. Eng. Chem.,* **21,** 594 (1929); see also Fukushima, I., Horio, M., and Miki, T., *J. Soc. Chem. Ind. Japan,* **35,** 142 (1932); *Chem. Abs.,* **26,** 3939 (1932).

[33] Rose, C. H., and Bolley, D. S., *Ind. Eng. Chem.,* **28,** 115 (1936).

[34] Clark, G. L., and Tschentke, H. L., *Ind. Eng. Chem.,* **21,** 621 (1929). A Mazda lamp source is used by Nicolson, D. G., and Holley, C. E., Jr., [*Ibid.,* **30,** 563 (1938)], who believe light destroys an inhibitor.

greatest after ultraviolet treatment. Although sunning requires hours, ultraviolet aging takes only minutes.

Auer [35] suggests treatment of linseed oil or castor oil with peroxides (*e.g.,* those of Mg, Zn, Ce or Na) and by heating at 250 to 300°C. under vacuum to obtain products which can be vulcanized and used as rubber substitutes. They may be employed also in the form of emulsions or as ingredients of varnishes, linoleum compositions, etc. In some cases, the products are further improved by exposure to ultraviolet rays or x-rays and by the use of such secondary reagents as formaldehyde, phenol, thiocarbanilide, benzidine, etc.

Experiments on the oxidation and polymerization of soybean oil were carried out by Taverne.[36] After ten days of exposure in air at room temperature, by Fahrion's method, the hydroxy-acids of three grams of oil on ten grams of cotton yarn were found to be 38.4 per cent. At 70° C., in the apparatus of Genthe [37] the oxidation was complete in thirty hours. By heating the irradiated oil in a beaker at 150° C., the molecular weight rose in ten days from 710 to 1730, indicating that polymerization accompanies oxidation. The oil became solid and contained 31.8 per cent hydroxy-acids and 63 per cent fatty acids soluble in petroleum ether, while the iodine number decreased to 64.8. Although Genthe had claimed that siccative oils can be bleached without oxidation, there was complete oxidation in 45 hours in Taverne's experiments. A lead (6.28 per cent) manganese (5.76 per cent) rosin compound was found to be the most active agent for hastening oxidation. On exposure to ultraviolet at 70°C., oxidation was complete with 5 per cent siccative oils in about ten hours.

Inaba, Kitagawa and Sato, and also Shinozaki and Sato,[38] exposed alcohol-extracted and benzine-extracted pressed soybean oils, both crude and refined, to ultraviolet light for sixty hours. After twenty hours, the alcohol-extracted and refined pressed oils were almost water-white, but it took thirty-five hours to decolorize crude pressed oil and benzine-extracted oil. Red colors were more easily bleached than yellow. The density, relative viscosity and refractive index increased with the time of exposure, sharply after fifty hours. For the first thirty hours the acid values remained constant, but after sixty hours they attained four to fifteen times their original values, reaching 4.5 to 5.5 no matter what they had been at the start. In the alcohol-extracted and refined pressed oils, the iodine numbers began to change after fifteen hours and in the benzine-extracted and crude pressed oils after thirty hours. After these periods, they decreased gradually. Fifty hours of exposure produced a substance soluble in petroleum ether; this amounted to 10 to 16 per cent after sixty hours. After 55 hours, the water-insoluble acids decreased by 2 to 5 per cent and the unsaponifiable matter increased 0.4 per cent. The oxygen content of the oils increased 4 to 5 per cent after ten hours. Both original and treated oils gave a weight increase of 6 to 7 per cent after 33 days. The ultraviolet absorption spectra also changed during the treatment, the oils becoming more opaque to the ultraviolet and less so to the visible rays.[39]

The carbon arc greatly accelerates the drying of various oils. Perilla oil set

[35] Auer, L., U. S. P. 1,980,366, Nov. 13, 1935; *Chem. Abs.,* **29,** 254 (1935); see also French P. 652,796, Oct. 4, 1926; *Chem. Abs.,* **23,** 3804 (1929). British P. 321,690, 1929.

[36] Taverne, N., *Z. angew. Chem.,* **28,** (I), 249 (1915).

[37] Genthe, A., German P. 223,419, Aug. 24, 1907; *J. Soc. Chem. Ind.,* 1168 (1910); *Chem. Abs.,* **4,** 3146 (1910). In this, the oil or fat at 70-90°C. is treated with rays from an immersed mercury arc while air is blown through the hollow arm of a stirrer. It is claimed that 1000 kilos of linseed oil can be bleached with an expenditure of 60 k.w. hours for current, 30 h.p. hours and 1500 cubic meters of compressed air for stirring.

[38] Inaba, T., Kitagawa, K., and Sato, M., and Shinozaki, Y., and Sato, M., *J. Soc. Chem. Ind. Japan,* **37,** 372, 374 (1934); *Chem. Abs.,* **28,** 7046 (1934).

[39] For further studies of the influence of air, oxygen, hydrogen peroxide, diffused daylight, direct sunlight and ultraviolet light on the physical properties and oxidation of soybean oil, see Horovitz-Vlasova, L. M., Katschanova, E. E., and Tkatschev, A. D., *Z. unters. Lebensm.,* **69,** 409 (1935).

to touch in two hours.[40] Oils such as candlenut, poppyseed, menhaden and soybean set to touch in four to seven hours. The so-called semi-drying oils, corn, cottonseed and rubberseed, were found to dry in about 24 hours. Gardner[41] described apparatus suitable for drying newly painted walls.

In drying tests at the Institute of Paint and Varnish Research in Washington,[42] there is employed a metal drum revolving in thirty minutes and surrounding a low-pressure quartz mercury arc. In this apparatus perilla and linseed oils containing 0.02 per cent of cobalt became solid in 24 hours and tung oil in four hours. These products yield to hot acetone 20, 32 and 16 per cent, respectively, of unpolymerized products. The polymerized, sponge-like residues, after drying, were tested to determine the amount of a petroleum distillate they could absorb. That from perilla absorbed 70 per cent, from linseed oil 80 per cent and from tung oil 160 per cent of the mineral spirits before the surfaces of the particles appeared wet. These preliminary results indicated the possibility of producing these solid products from oil economically. Tung oil treated with 0.05 per cent sulfur produced a wax-like mass resembling a hydrogenated fat, which might be used in linoleum manufacture.

The yellowing of oxidized drying oils cannot be due to the presence or formation of ketohydroxy- compounds in the film, according to Elm and Standen,[43] since ketohydroxystearic acid is colorless, although diketostearic acid is yellow. From their appearances in filtered ultraviolet, the yellowing differs in tung and linseed oil films.[44]

Castor oil exposed to the sun in a thin layer solidifies fairly rapidly.[45] Polymerization of pilchard oil by ultraviolet rays shortens the induction period for its oxidation, and increases the rate of the process and the total amount of oxygen absorbed.[46]

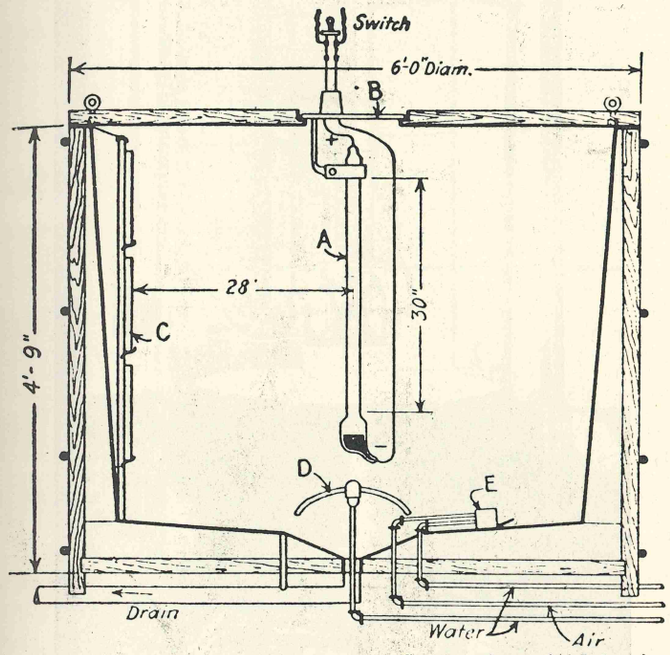
The densities, refractive indices and saponification numbers of sunflower-seed oil samples are gradually increased by ultraviolet irradiation. The acidity increases comparatively little, the iodine number drops toward the end of a series of thirty irradiations (2 to 6 hours) at ten-day intervals. The acetyl number at first rises and then drops. The oil is bleached considerably.[47]

When fully extracted oil of the kernels of *Telfairia occidentalis,* which contains α-eleostearic acid, is exposed to diffused light for some weeks, very small yields of the β-isomer are formed. The yield is greatly increased by exposure to ultraviolet rays for some hours.[48]

In the oil of the pits of the Brazilian oiticica tree, the chief constituent is licanic acid (4-oxo-9,10,11,12,13,14-octadecatriene-1-carboxylic acid), which resembles eleostearic acid in being extraordinarily sensitive to light and air. The three double bonds make possible the existence of eight isomers, of which two are known. The fresh oil contains α-licanic acid, as glyceride which when illuminated in the presence of a trace of iodine, gives β-licanic acid.[49]

[40] U. S. Bureau of Standards Notes, *J. Frank. Inst.*, **206,** 694 (1928).
[41] Gardner, H. A., *Am. Paint Varnish Mfrs. Assoc. Circ.*, **335,** *July* (1928), 592; **330,** 482 (1928); *Chem. Abs.*, **22,** 3539 (1928).
[42] *Ind. Eng. Chem.*, **22,** 378 (1930).
[43] Elm, A. C., and Standen, G. W., *Ind. Eng. Chem.*, **24,** 1044 (1932).
[44] Eibner, A., *Paint Varnish Production Mfr.*, **14,** 7, 10, 14, 12, 30, March, 1936; *Chem. Abs.*, **30,** 2779 (1936).
[45] Sunder, C., *Bull. soc. ind. Mulhouse,* **102,** 353 (1936); *Chem. Abs.*, **30,** 7348 (1936).
[46] Denstedt, O. F., and Brocklesby, H. N., *J. Biol. Board Can.*, **1,** No. 6, 487 (1936); *Chem. Abs.*, **30,** 2784 (1936).
[47] Kozin, N. I., and Fridlyanskaya, F. M., *Masloboino Zhirovoe Delo,* **12,** 529 (1936); *Chem. Abs.*, **31,** 5191 (1937).
[48] Farmer, E. H., and Paice, E. S., *J. Chem. Soc.*, 1630 **(1935).**
[49] Brown, W. B., and Farmer, E. H., *J. Chem. Soc.*, 1632 **(1935).**

Pigments. The effect of ultraviolet light on the darkening of lithopones has been discussed in Chapter 21. Some application has been made of ultraviolet-induced fluorescence methods in the determination[50] of the nature and quality of pigments, but many variable factors exist and careful control and considerable experience are necessary. The method is said to be valueless for estimating the pigment value of lithopones or zinc white, but natural and precipitated chalks may be distinguished by their appearances in ultraviolet light.[51] The presence of 25 per cent of zinc oxide in titanium white changes the violet fluorescence of the latter to a greenish yellow. The admixture of organic coloring matters in mineral pigments can frequently be detected by this method.



Courtesy Automotive Industries

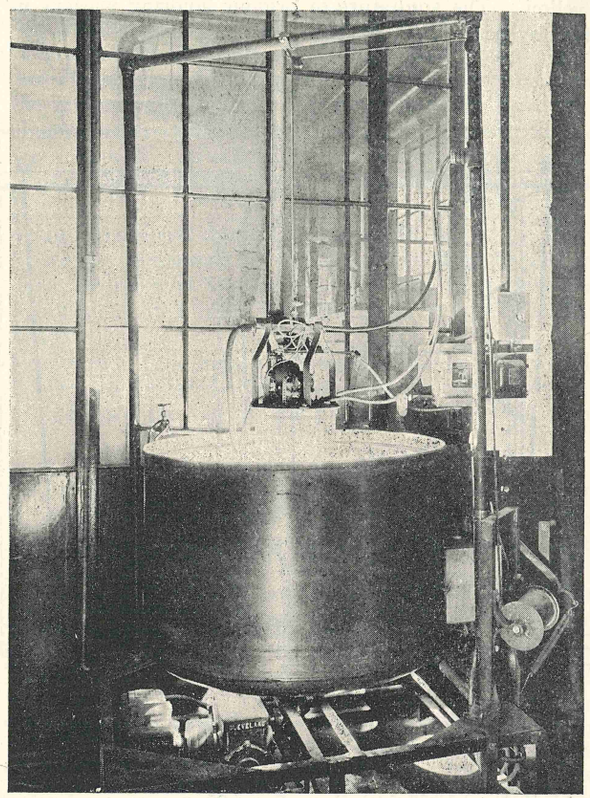
FIGURE 125. Nelson Exposure Tank.

Kurotaki and Kobayashi[52] introduce 5 to 20 per cent of trivalent nitrogen organic compounds without acyl, alkyl or alkylene groups or their aldehyde condensation products in order to increase the light-fastness of pigments. Among the compounds used are α-naphthylamine, phenylenediamine, phenylazobenzene, phenylhydrazine and diazoaminobenzene.

The one salutary effect of light on paints is its bleaching action on yellowed surfaces. Whereas light of wave-length 3200A or less is required to produce pronounced deterioration of paints and darkening of lithopones, the beneficial bleach-

[50] Kufferath, A., *Farbe und Lack,* 473 (1935); Grant, J., *Oil and Colour Trades J.*, **85,** 1601 (1934); *Chem. Abs.*, **28,** 5997 (1934); *Paint Manuf.*, **7,** 340 (1937); Elm's, J., *Rev. gén. mat. plastiques,* **14,** 154 (1938); Bandel, G., *Angew. Chem.*, **51,** 570 (1938).
[51] Schoen, M. J., and Rinse, J., *Chem. Weekblad,* **26,** 321 (1929); *Brit. Chem. Abs.* **B,** 609 (1929).
[52] Kurotaki, S., and Kobayashi, C., Japanese P. 110,746, May 13, 1935; *Chem. Abs.*, **30,** 2411 (1936).

ing action extends to much greater wave-lengths, in fact, up into the visible spectrum, according to some qualitative observations of Pfund.[53] On the other hand, in the case of nitrocellulose lacquers, the addition of any such plasticizers as dibutylphthalate, tricresyl phosphate, Sipalin AOM and Sipalin MOM increases the yellowing of the films on exposure to ultraviolet light, the effect being greatest with tricresyl phosphate, next with butylphthalate, next with Sipalin MOM and least with Sipalin AOM.[54]



Courtesy National Carbon Co., Inc.

FIGURE 126. Paint and Varnish Test Using Eveready C_3A Unit.

Accelerated Weathering Tests.[55] Accelerated weathering tests for paint films have been devised by many, and usually involve the use of some ultraviolet light source to bring about in a short time the effects of sunlight over a prolonged period. It is readily apparent that there should be no reason to expect the short

[53] Pfund, A. H., *Proc. Am. Soc. Testing Materials,* **23,** *II,* 377 (1923).

[54] Wolff, H., and Rosen, B., *Farben Ztg.,* **34,** 2564 (1929); *Chem. Abs.,* **23,** 4835 (1929).

[55] A brief account of the historical development of accelerated paint tests has been given by Würth, K., *Farben Ztg.,* **33,** 1470 (1928). For a general discussion of radiation and paint, see New, G. F., *Paint Manuf.,* **6,** 145-6; *Oil Colour Trades J.,* **89,** 787 (1936), and Masseille, H., *Peintures, pigments, vernis,* **8,** 1478 (1931).

wave-length, highly active radiations to produce effects similar to those of the longer wave-lengths present in sunlight. Nevertheless, when their limitations are borne in mind, the use of ultraviolet tests may furnish in a short time comparative data which may be useful although they may not be in complete agreement with the results of prolonged fading tests.

Nelson[56] used a wooden exposure tank surrounded by an insulated air-space and lined with galvanized iron and containing a cylinder which revolves the test panels in a 24-hour cycle. Effects of sunlight, rain and mist were simulated by a quartz mercury arc, a revolving spray and a water-atomizer, respectively, together with a variable-speed electric fan to cool the arc and maintain a uniform temperature. (See Figure 125.) A more recent testing tank employs a carbon arc. (Figure 126.)

A cycle of exposure for 24 hours to the rays of the arc at a temperature of 50 to 60°C., followed by cooling and exposure to the water spray for another 24 hours at 5 to 10°C. was chosen as representing actual service conditions. Exposures were made at a distance of 28 inches from the source of the rays, investigation proving that the useful rays of destructive effect had a wave-length in the neighborhood of 3000A. On an average, comparable results were obtained in as many days in the apparatus as in months under service conditions. The following results were obtained on a series of paints, the figures referring to the number of days necessary for complete loss of gloss, and for initial chalking, respectively: 100 per cent lead-free zinc oxide, 14, 16; 100 per cent leaded (35 per cent) zinc oxide, 9, 12; 100 per cent light-resistant lithopone, 4, 6; 100 per cent basic lead carbonate, 3, 5; 100 per cent Titanox, 2, 4; a mixture of 40 per cent zinc oxide, 40 per cent lithopone, 20 per cent whiting, 9, 11. The effect of periodic saturation and maintenance of a saturated atmosphere during exposure is to accelerate both complete loss of gloss, and initial chalking by 50 per cent. Freezing of a saturated film materially promotes the formation of removable "chalk," most probably due to the formation of ice within the film. Neither flaking nor checking was reproduced in any of these tests. Cracking, rapidly followed by scaling and peeling, is produced by periodic exposures to temperatures considerably below freezing point, and is reproducible by exposures of equal alternate intervals to radiation, low temperature, and water-spray for a period of 100 days, equivalent to 14 to 15 months' exposure to the weather. Lack of adherence is a fault more strictly connected with the method of application of the paint, but can be brought about by exposure at 50 to 60°C. to the mercury arc. Of commercial paints intended for use as protective coatings for iron, both a 100 per cent red-lead paint and a mixture of 85 per cent ferric oxide with 15 per cent zinc oxide showed outstanding merit in maintaining gloss and inhibiting the formation of rust as compared with iron oxide paints containing various fillers, and a zinc oxide sublimed lead paint also containing a filler. Although a certain light-resistant lithopone maintained its whiteness over a period of three years on exterior exposure, the effect of the ultraviolet radiations was to discolor both this product and white lead in a short time.

Films exposed to ultraviolet rays increase in tensile strength and decrease in extensibility.[57] This effect is less pronounced with films containing zinc oxide, which is opaque to ultraviolet rays, than with films containing basic carbonate white lead, which is more transparent. The hardening and subsequent disintegration of the surface of a linseed-oil binder through reactions induced by ultraviolet radiation must be recognized as a fundamental cause for the failure of paints by chalking. This effect may be reproduced on pigments such as basic carbonate white lead by ultraviolet exposure alone without introducing any temperature or moisture variations.

Verification of the deteriorating effects of ultraviolet light came quickly from a number of sources. Thus, Wagner[58] claimed that the quartz mercury-vapor

[56] Nelson, H. A., *Proc. Am. Soc. Testing Materials* **22,** II, 485 (1922).

[57] Nelson, H. A., and Rundle, G. W., *Proc. Am. Soc. Testing Materials,* **23,** II, 356 (1923); *New Jersey Zinc Co., Research Bull.,* March, 1930.

[58] Wagner, H., *Farben Ztg.,* **30,** 2991 (1925); *Chem. Abs.,* **19,** 3602 (1925); *Farben Ztg.,* **31,** 1023, 1073 (1926); *Z. Angew. Chem.,* **38,** 1191 (1935).

lamp gives the same final bleaching of 14 mineral pigments and 75 coal tar dyes as sunlight in one-fifth to one-thirtieth of the time, but noted that the type and quality of the vehicle influenced the results. The refractive index of the binding medium should be as near as possible to that of the pigment. In testing organic pigments or dyes, the least favorable medium for determining fastness to light is an aqueous glue wash, and the most favorable an oil or concentrated dextrin medium. The conversion factor of ultraviolet lamp hours into sun hours differs widely for different pigments.

Discrepancies between the results of accelerated tests and outdoor exposures gradually became apparent. Gardner and Parks[59] believed that, regardless of whether the accelerated test wheel would determine how a coating will wear on exterior exposure, it is of great value in securing quick data in regard to the comparative aging of experimental coatings. Furthermore, as Dean pointed out,[60] the results of outdoor exposure tests are subject to factors difficult to control, such as climate, temperature range and the rate of its variation, rainfall, humidity, wind, abrasive dusts and various gaseous contaminants of the air. This accounts for the effort spent by many workers in developing the better controlled accelerated testing methods.

Nelson and Schmutz[61] balanced the weathering factors used in their tests to approximate at least roughly the order and relative magnitude of these factors as they appear in average outdoor weathering conditions. The weathering of a paint, varnish or lacquer surface may be considered a process of (1) rendering the film indistensible or (2) bringing about internal strains due to shrinkage, or both, and then of (3) revealing these weaknesses by the breaking up of the surface. The first of these usually involves oxidation, condensation and chemical decomposition. The second is usually due to temperature changes, which, in an indistensible film can be compensated for only by cracking and peeling.[62]

The apparatus of Nelson and Schmutz[63] consisted of a circular exposure tank four feet in diameter and sixteen inches in height with the destructive light source at the hub. A water spray, a silica gel dehydrator, and heating and cooling coils were included in an air-circulating system. Gas inlets and outlets for the introduction of oxygen and ozone when desired were provided. Refrigeration and water spray exposures were carried out in separate units, although it was also possible to use the water spray in the light exposure chamber. As a source, the flaming arc of the Atlas Electric Devices Co. Fade-Ometer was preferred to the quartz mercury arc since its spectrum more closely resembles that of the sun. It has approximately 34 per cent of its intensity below 4100A but none below 3100A. In comparative tests employing the mercury arc and the treated carbon arc in similar cycles, panels with three coats of a house paint lost 76 per cent in gloss and chalked badly with the mercury arc; they lost only 13 per cent in gloss and did not chalk with the carbon arc. The temperature should be 140°F. and certainly not higher than 160°F. Although light exposures accompanied by high humidity might be expected to show great destruction, most failures such as chalking and checking, were noted during light exposures at low humidity when given immediately after high humidity exposures. From stress-strain measure-

[59] Gardner, H. A., and Parks, H. C., *Paint Mfrs. Assoc., U. S. Circular* **232**, 248 (1925); *Chem. Abs.*, **19**, 2560 (1925).

[60] Dean, H., *Chemicals* (Oct. 25, 7, 1926).

[61] Nelson, H. A., and Schmutz, F. C., *Ind. Eng. Chem.*, **18**, 1222 (1926).

[62] Erosion is rarely considered. See Nelson, H. A., and Werthan, S., *Ind. Eng. Chem.*, **18**, 965 (1926).

[63] Nelson, H. A., and Schmutz, F. C., *Proc. Am. Soc. Testing Materials*, **26**, II, 563 (1926); Nelson, H. A., Schmutz, F. C., and Gamble, D. L., *Ibid.*, **26**, II, 1 (1926).

ments on paint films, adsorbed water generally increases distensibility. Therefore, severer deteriorations may actually be taking place during a light exposure with high humidity but will not be so quickly revealed because of the additional distensibility induced by the adsorbed water. In a subsequent light exposure with low relative humidity, the previous weakening of the films shows up because the surface in the dry condition has a lower distensibility. This influence of humidity varies with the water resistance of the surface tested. In general, the humidity of the light exposure chamber should be made to conform to the ratio of high to low humidity conditions of the weather simulated. Checking, which was formerly difficult to reproduce in characteristic form, is promoted by the addition of oxygen up to 30 or even 100 per cent. In routine testing, 30 per cent is adopted. The temperature of the water spray is also of importance.

One month in a suitable weathering cycle should approximate fourteen months of outdoor exposure, when a suitable addition of oxygen is made.

The Bureau of Standards employed[64] a flaming carbon arc. The regular test program is made up of exposure to ozonized air for three hours, rain for three hours, light for seventeen hours and inspection one hour. In addition, on three days each week, the panels are subjected to refrigeration at −23°C. for one hour, one-half hour being subtracted from the periods for exposure to ozone and rain. The order of exposures is varied on different days.

In a more recent description of the Bureau of Standards method, Hickson and Walker[65] state that the chamber for exposure to light and moisture consists of a rotating cylinder made of No. 16-gauge galvanized iron 76 cm. in diameter, 38 cm. high, open at both ends with the light-source suspended in the center. This size was selected to bring the light as near the panels as possible, at the same time avoiding too high temperatures. The cylinder has a capacity for sixty 7.5×15 cm. panels. These are placed in two tiers immediately opposite the light inside the cylinder, the panels thus being 38 cm. from the center of the light source. This gives a temperature of about 50 to 55°C. at the panels with the type of lamps used. Thirty slotted holders 7.5 cm. wide and about 35 cm. long for the panels are attached to the open surface of the open cylinder. A pan placed about 5 cm. below the bottom of the light cylinder contains water and serves to keep the temperature next to the panels down to about 52°C. as well as to humidify the air. To duplicate sunlight reasonably, an enclosed type carbon arc light operated at 220 volts d.c. and 13 amps. is employed. On each renewal of the carbons, the glass globe (opaque to wave-lengths less than 3200A) should be cleaned. To simulate a hot, humid climate, a fixed water spray is mounted in the tank in such a manner that it may function while the lights are operating. The light cylinders rotate slowly at three revolutions per hour. An ammonia coil about $27 \times 47 \times 40$ cm. in an insulated chamber that can be cooled to −25°C. is used to chill the panels quickly. On removal from the light chamber, the test panels are placed in racks and the rack and samples are placed in the refrigerator, left there for one hour and then removed.[66]

In a method employed in Germany by Schulz[67] the paints are applied to iron plates and allowed to dry for at least three days, then matured for 24 hours at 80°C. The subsequent treatment consists of six repetitions of the following cycle: hanging in distilled water at 20°C., exposure to ultraviolet light while moist and again when dried,

[64] *Tech. News Bull., Bureau of Standards*, Sept. 4, 1927; Walker, P. H., *International Congress Testing Materials*, II, 603, 1927; *Chem. Abs.*, **23**, 997 (1929).

[65] Hickson, E. F., and Walker, P. H., *Ind. Eng. Chem.*, **20**, 591 (1928).

[66] Note also Davidson, J. G., and Reid, E. W., *Ind. Eng. Chem.*, **20**, 199 (1928).

[67] Schulz, M., *Farben Ztg.*, **31**, 2879 (1926); *Brit. Chem. Abs.*, **B**, 924 (1926); *Farben Ztg.*, **32**, 2128 (1927).

re-immersion in distilled water, enclosure in a damp atmosphere containing carbon dioxide, further exposure to ultraviolet light under damp conditions, and then at 50°C., enclosure in an atmosphere containing sulfur dioxide, exposure to damp air at 35 to 40°C., with interpolated periods at −5°C., and renewed action of ultraviolet rays. It was claimed that the results on zinc oxide-lithopone paints showed agreement with a two-year exposure to the atmosphere, in that the iron plates showed increasing rusting with the increase in proportion of lithopone to zinc oxide in the protecting paint.

In a rapid-testing apparatus described by Blom,[68] two parallel chains are mounted on tiers of cog-wheels two meters apart so as to carry between them fifty test sheets 10×20 cm. The chains travel at 20 cm. per minute and carry the sheets through three heating chambers and one freezing box. Sprays are fitted between the chambers, one of which can be filled with corrosive gases if desired. The strips are also submitted to both ultraviolet light and the light from a Sollux lamp. A typical time of treatment is only five days. Another German test machine described by Ritter[69] is claimed to give results in from 32 to 60 hours. An accelerated test has been patented by Digby, King and Kelvin, Bottomley and Baird, Ltd.,[70] and others have been described by Walter[71] and by Vila.[72]

Inconsistencies between the results obtained by the ultraviolet methods and outside exposures have led to renewed study of the effects of various light sources. Zeidler and Toldte[73] exposed eleven paints with various lead pigments on iron panels to radiations from the sun, an arc light, a mercury arc and a Nitra lamp, in some cases with a previous exposure to the action of hydrogen sulfide. The relative effects of the various sources on different paints were not uniform. In general, the mercury arc effected the greatest degree of fading of the discoloration produced by hydrogen sulfide.

Schmutz and Gamble[74] investigated the effects of six impregnated carbon arcs of known spectral energy distribution, the untreated carbon arc and the mercury arc on lithopones in nitrocellulose lacquers. Intensification of the infrared and visible ranges had but little influence on the results. One sample was unaffected by intensification between 3200 and 4200A. Two others were equally affected, although rays between 3000 and 3200A brought out a difference between them, and caused some effect on a third sample unaffected by the longer rays. With radiations below 3000A, the darkening was the same in the sample not affected at the longer wave-lengths and in only one of the two which had been equally affected by the longer rays. All samples showed up poorly. It is evident that specific wave-lengths exert specific effects on various samples of the same type of pigment. When wave-lengths shorter than 2500A are employed, the differences between samples become less marked.

The chief difficulty in the use of the carbon arc is due to the heat generated, elaborate cooling systems being required for its use in closed systems. Preliminary experiments indicated that the suitability of the mercury arc for this work could be increased by the employment of filters of Corning glasses.[75] Vitrified quartz burners were believed to have the advantage of not completely transmitting the far ultraviolet and of being more rugged than fused quartz.

[68] Blom, A. V., *Chem. Fabr.*, 102 (**1928**); *Chem. Abs.*, **22**, 3789 (1928).

[69] Ritter, E., *Kali*, **23**, 10, 26 (1929); *Chem. Abs.*, **23**, 2048 (1929).

[70] Digby, W. P., King, F. A., and Kelvin, Bottomley and Baird, Ltd., British P. 429,792, June 6, 1935; *Chem. Abs.*, **29**, 7100 (1935).

[71] Walter, P., *Bull. soc. encour. ind. natl.*, **134**, 213 (1935); *Chem. Abs.*, **29**, 5287 (1935).

[72] Vila, A., *Recherches et inventions*, **16**, 26, 349 (1935); *Chem. Abs.*, **29**, 6441 (1935).

[73] Zeidler, G., and Toldte, W., *Farben Ztg.*, **33**, 1507, 2607 (1928); *Chem. Abs.*, **23**, 3585 (1929); *Farben Ztg.*, **34**, 1547 (1929); *Brit. Chem. Abs.*, **B**, 365 (1929).

[74] Schmutz, F. C., and Gamble, D. L., *Ind. Eng. Chem., Anal. Ed.*, **1**, 83 (1929); see also Gardner, H. A., and Sward, G. G., *Am. Paint Varnish Mfrs. Assoc., Circular 358*, 64 1930; *Brit. Chem. Abs.*, **B**, 622 (1930); Nelson, H. A., *First Communications, New International Assoc. Testing Materials, Zurich*, 117 (1933).

[75] See also Becker, E., *Farben Ztg.*, **33**, 2232 (1928); *Chem. Abs.*, **23**, 1290 (1929).

Sward and Hart[76] compared the outdoor weathering of a number of coating materials with that produced by (1) a pair of 13-amp. enclosed carbon arcs, (2) a 50-amp. flaming carbon arc with Sunshine carbons, (3) a similar one with therapeutic C carbons and (4) a low-pressure mercury in quartz arc. Typical outdoor-type failures were obtained with the first and second sources, the latter being two to three times faster than the former. Failure by chalking predominated with the third and fourth even in materials which out-of-doors failed by checking. A combination of sources might be used to produce both checking and chalking. The operating costs are approximately 22, 21, 21 and 8.5-13 cents per hour for the four sources, exclusive of capital investment.

There has been much general discussion of the applicability of these accelerated methods. Grunder and Shepherd[77] believed them useful in comparing colors of the same basic type. The need for more refined methods for detecting failures has frequently been emphasized.[78]

The accelerated tests have the advantage of rapidity, constancy of results and ready adaptability to simulate peculiar exposure conditions.[79] Nettmann,[80] who is somewhat more critical of their value, attempted a theoretical discussion of the aging of paints on the basis of accumulation of potential energy in the films being responsible for changes in their inner structure. Nauroy[81] pointed out that no accelerated aging test could give the paint user an absolute or even a comparative measure of the value of a product submitted to him. Nevertheless, such tests can be of considerable value to the manufacturer for rapid control of the effects of variations in formulas. Williams[82] exposed panels of various yellow and green paints to ultraviolet light for 150 hours at 16 inches from the light. Warm air at 34°C. was continuously circulated around the panels. Failure was a darkening, probably the result of a reaction between paint and vehicle. Very pronounced chalking resulted but no great difference was apparent between panels of the same group. Gardner made some studies[83] of the water-soluble material produced by the action of weathering and ultraviolet light on various paints.

Sieplein[84] plotted the duration, intensity and fluctuational characteristics of outdoor ultraviolet radiation effective in exposure tests from astronomical and meteorological data for Miami and for a point representative of the eastern industrial region of the northern United States. Gardner[85] notes that paint films prepared indoors and stored in confined spaces often develop a mottled appearance when later exposed out of doors to the action of the sun.

The literature of the behavior of white pigments toward ultraviolet light has

[76] Sward, G. G., and Hart, L. P., *Am. Paint Varnish Mfrs. Assoc. Circular 375*, 53 (1931); *Chem. Abs.*, **25**, 1105 (1931).

[77] Grunder, A., and Shepherd, R. S., *Paints, Oils Chem. Rev.*, **6**, No. 6, 8, 25 (1928); *Chem. Abs.*, **22**, 3538 (1928).

[78] Kempf, R., *Farben Ztg.*, **33**, 2359 (1928); *Brit. Chem. Abs.*, **B**, 578 (1928); Walker, P. H., and Hickson, E. F., *Ind. Eng. Chem.*, **20**, 591 (1928). Toldte, W., advocated the use of the Pulfrich stepphotometer and the Ostwald color system for reporting the effect of light on paints, *Farben Ztg.*, **39**, 140 (1934).

[79] Eibner, A., *Farben Ztg.*, **34**, 322 (1928); *Brit. Chem. Abs.* **B**, 63 (1929).

[80] Nettmann, P., *Farben Ztg.*, **34**, 2181 (1929); *Brit. Chem. Abs.*, **B**, 609 (1929); *Farbe und Lack*, 77, (**1931**); *Chem. Abs.*, **25**, 2009 (1931).

[81] Nauroy, A., *Chimie et industrie*, Special No. *683* (March, 1932); *Chem. Abs.*, **26**, 3681 (1932).

[82] Williams, J. J., *Am. Paint Varnish Mfrs. Assoc. Sci. Section, Circular 341*, 879 (1928); *Chem. Abs.*, **23**, 5334 (1929).

[83] Gardner, H. A., *Am. Paint Varnish Mfrs. Assoc. Circ. 313*, 368 (1927); "Physical and Chemical Examination of Paints, Varnishes and Lacquers," 4th ed., 183, 308, 1927.

[84] Sieplein, O. J., *Natl. Paint Varnish Lacquer Mfrs. Assoc., Circular No. 447*, 1, (1934); *Brit. Chem. Abs.* **B**, 209 (1934).

[85] Gardner, H. A., *Natl. Paint Varnish Lacquer Mfrs. Assoc. Circular No. 455*, 66 (1934); *Chem. Abs.*, **28**, 3251 (1934). He describes an outdoor water-wheel test rack. *Natl. Paint Varnish Lacquer Assoc., Sci. Section, Circular 534*, 177 (1937); *Chem. Abs.*, **32**, 3639 (1938).

been reviewed by van Hoek.[86] Wagner[87] states that the inferiority of the chalk paints to those made from barium or calcium sulfates is not due to their impermeability to ultraviolet light, which is about equal to that of paints with barytes and other white bases, but appears to be due to the flocculated condition of the chalk particles in the prepared paint, to the fineness of the particles, to their soft texture, to the high oil content of the paint and to its great tendency to swell. The usual discoloration of titanium white paint is ascribed by Zhukova and Sovalova[88] to the instability of the titanium dioxide-linseed oil system because of poor wettability of the oxide by the oil. By using an oxide ignited at 800°C. instead of at 600°C., the discoloration in darkness is greatly retarded and that in ultraviolet light is practically eliminated. Soaps have a similar effect by forming pigment-enveloping aggregates which prompt the dispersion of the oxide in the medium.

It is difficult to increase the fastness of chromes without adversely affecting the desirable properties of greening power or tinctorial strength and brightness of shade.[89]

To understand the susceptibility of various paint films to ultraviolet light, it is necessary to know something of the absorption of the harmful radiations by the pigments, since if they are so absorbed, there will be less energy to be absorbed by the oxidized oil film and less resulting deterioration of the film. At the same time, it is also desirable to know the relative abilities of various pigments, fillers and paint films themselves to reflect ultraviolet light. This is of some importance in the development of special paints for covering walls of rooms in which dual-purpose lighting is used.

Pfund[90] estimated the coefficients of diffused reflection from dry pigment surfaces by calculation from photographic records obtained by allowing the light reflected by a pigment surface from a small quartz mercury arc to enter the slit of a small concave grating spectrograph. When light falls on a thick layer of fine particles it penetrates a large number of particles before being returned, so that the reflection coefficients give roughly qualitative results for the opacities of the pigments examined. Zinc oxide became practically opaque near 3600A; basic carbonate white lead was by far the most transparent pigment examined. "Titanox," Timonox, lithopone, and sublimed white lead fell between these limits. Powdered sulfur is very opaque. Fused magnesia has constant reflecting power throughout the ultraviolet spectrum. In general, sulfur and zinc oxide are the most effective pigments in removing radiations harmful to the film. The inerts are the least effective. From studies of mixtures with a volume ratio of pigment to vehicle of 1:60 in films 0.065 mm. thickness, determinations of the decreased transmission due to pigment placed the transparencies of the pigments in the same relative positions as the determination of the diffused reflection coefficients. The transmission of the inert pigments is very high and is nearly non-selective.

Hallett[91] attacked the same problem in a somewhat different manner. The light from a quartz mercury lamp, after passing through a suitable glass filter to remove practically all the visible spectrum, passed through a quartz lens onto the painted surface from which it was either reflected or transmitted to sensitized paper.

[86] van Hoek, C. T., *Farben Ztg.*, **34**, 833, 895, 954, 1006 (1929); *Brit. Chem. Abs.*, **B**, 180 (1929).
[87] Wagner, H., *Farben Ztg.*, **34**, 2011 (1929); *Brit. Chem. Abs.*, B565 (1929).
[88] Zhukova, A., and Sovalova, A., *Za Lakokrasochnuyu Ind.*, No. 2, 11, 1934; *Chem. Abs.*, **29**, 3859 (1935).
[89] Barker, J., *Oil, Colour Trade J.*, **87**, 575 (1935); *Chem. Abs.*, **29**, 7675 (1935).
[90] Pfund, A. H., *Proc. Am. Soc. Testing Materials*, **23**, II, 369 (1923).
[91] Hallett, R. L., *Proc. Am. Soc. Testing Materials*, **23**, II, 379 (1923); *Chem. & Met. Eng.*, **29**, 64 (1923).

The paper was developed and the degree of blackening determined by measurements with a Howland color photometer, and calculated to the "Arturascale," in which the unexposed paper is taken as zero and the completely exposed paper as 100 per cent black. The values in per cent reflected, transmitted and absorbed by paints containing the following pigments (all in the same volume relation to the vehicle) are: Basic carbonate white lead, 42, 4, 54; zinc oxide, 0, 0, 100; basic sulfate white lead, 3, 0, 97; Titanox, 16, 0, 84; lithopone, 36, 1, 63; red lead, 1, 0, 99; iron oxide, 1, 0, 99; lamp black, 2, 0, 98. Further observations are due to Stutz.[92] New,[93] however, finds it impossible to predict from the transmission and reflection coefficients of pigments their effect on the durability of paint films exposed to ultraviolet radiation. In general, white paints are superior to aluminum paints in reflecting sunlight and in cooling power. Wagner and Pabst[94] find even thick films of white lead highly translucent to visible and ultraviolet light. Red lead is also transparent in thin but not in thicker layers. The addition of 50 per cent barite increases the translucency about 20 per cent. Finely dispersed hammerscale or lead reduction scale renders films opaque. Zinc white, so-called molybdate red lead, and iron oxide with zinc white or zinc chromate impart ultraviolet opacity.

The possibility exists that a pigment which absorbs energy may become excited thereby and may then pass over some of this energy of excitation to the film components. Goodeve[95] states that zinc and titanium oxides, which exhibit a steep fall in reflecting power at 3850 and 4000A, may serve as sources of photoactivation for the oxidation of oil vehicles or for the bleaching of adsorbed dyestuffs. He finds, however, that zinc oxide does not cause the oxidation of linseed oil, although titanium oxide does. The reduction of chalking by zinc oxide is a specific effect, attributed to internal filter action. Goodeve has also given the diffuse reflecting power of other materials such as lead carbonate, barium sulfate, magnesium carbonate and silica.

Luckiesh and Holladay[96] state that casein and nitrocellulose lacquer can be used as binders for ultraviolet reflecting paints, and that these should preferably contain a large proportion of magnesia, magnesium carbonate, alumina, or a mixture of these. Moderate amounts of silica, calcium carbonate, china clay and asbestine may be added without greatly reducing the reflecting power, which is about 5 to 65 per cent.

Lighting by luminous paints is proposed by Risler[97] A surface coated with a luminous paint containing a phosphorescent sulfide is rendered continuously luminous by subjecting it to the rays of the spectrum ranging from blue to ultraviolet. To obtain the rays, a vacuum tube activated by high-frequency currents and filled with gas, such as nitrogen, argon or air, is preferably used. In a modification of the process,[98] a vacuum tube with or without electrodes and filled with rarefied gas such as argon, nitrogen or air is coated internally or externally with a luminous paint containing a phosphorescent sulfide, or having the sulfide incorporated in the glass of the tube, whereby a continuous luminous effect is obtained. The sulfides may be mixed with a varnish and the luminous coating is preferably covered with an impermeable and fireproof coating comprising cellulose acetate, alcohol, triacetin, acetone and tetrachloroethane (see also Chapter 8).

[92] Stutz, G. F. A., *J. Frank. Inst.*, **200**, 87 (1925); **202**, 89 (1926); *Ind. Eng. Chem.*, **19**, 897 (1927).
[93] New, G. F., *J. Oil and Colour Chem. Assoc.*, **19**, 156 (1936); *Chem. Abs.*, **30**, 8652 (1936).
[94] Wagner, H., and Pabst, E., *Farben Ztg.*, **42**, 664, 691 (1937); *Chem. Abs.*, **31**, 8952 (1937); Kessler, *Farben Ztg.*, **43**, 39 (1938); *Chem. Abs.*, **32**, 4360 (1938).
[95] Goodeve, C. F., *Trans. Faraday Soc.*, **33**, 340 (1937).
[96] Luckiesh, M., and Holladay, L. L., *J. Frank. Inst.*, **212**, 787 (1931); *Chem. Abs.*, **26**, 5218 (1932).
[97] Risler, J., British P. 207,786, 1923.
[98] Risler, J., British P. 208,723, Dec. 20, 1923.

Synthetic Resins

Before discussing the applications of ultraviolet in the preparation and testing of varnishes, the relations of radiations to the artificial resins will be considered.[99] Some polymerization reactions employed in the preparation of vinyl resins have been mentioned in Chapter 23. Ramstetter[100] carried out the condensation of carbamide or its derivatives and formaldehyde under the influence of radiation of short wave-lengths, *e.g.*, from a quartz mercury lamp, in the presence or absence of condensing agents. The rays were applied during the whole or part of the reaction or during the concentration of the reaction solution or the hardening of the product. In one example, a solution of carbamide is treated at 75°C. with a mixture of 80 per cent formic acid and 30 per cent formaldehyde at 40°C. and heated for a quarter hour under reflux while being irradiated. Excess of formaldehyde is distilled off under reduced pressure at 40°C. till a syrup remains and the latter is poured into flat molds. On keeping, it finally forms transparent flexible flakes, the hardening process also being accelerated by exposure to ultraviolet light. Geisel[101] states that the hardening is accelerated and that a tendency to cloud or deposit is counteracted if the mass is subjected to the action of ultraviolet light. Shono[102] found a phenol-formaldehyde resin to be decolorized in proportion to the amount of the ultraviolet rays (3190-2585A) to which it was exposed. Most resins made from the condensation products of phenols and aldehydes present the difficulty of discoloration by light. The urea-formaldehyde resin has, however, been found relatively light-stable.[103]

A substitute for drying oils as a medium for paints, varnishes, and impregnating agents for fabrics, wood, etc., proposed by Röhm,[104] consists of a solution of polymerized acrylic acid ester in acetone, lower fatty acids or other solvents. When exposed to sunlight or ultraviolet light, the ester is transformed into a colorless, transparent, tough mass, soluble in solvents for oils.

The polymerization of the methacrylates is furthered by heat, light, oxygen and peroxides. These resins have extreme ultraviolet transmission and excellent light stability.[105] Wave-lengths shorter than 2200A decompose methyl-methacrylate vapor, but longer ones polymerize it to a white solid. Once started by light, the polymer continues to grow in the dark for several days. This growth is proportional to the area of the tube irradiated and the pressure of the vapor.[106]

Furfural resins have a good black color and completely absorb ultraviolet rays. By adding a suitable amount of Bakelite resin, they can supply a very fine ebonite-like insulating material or an effective coating varnish which protects ebonite from ultraviolet rays.[107]

In preparing lacquers in which a resin fast to sunlight or ultraviolet light is

[99] Fluorescence tests for the identification of resins have been tabulated by Wagner and Schirmer. Wagner, H., and Schirmer, H., *Farben Ztg.*, **43,** 131, 157 (1938); *Chem. Abs.*, **32,** 4361 (1938).

[100] Ramstetter, H., German P. 416,252, Jan. 31, 1923; *Brit. Chem. Abs.*, **B,** 99 (1926).

[101] Geisel, W., German P. 437,646 (1924); *Brit. Chem. Abs.*, **B,** 452 (1927).

[102] Shono, T., *J. Soc. Chem. Ind. Japan*, **30,** 143 (1927); see also *Chem. Abs.*, **20,** 2729 (1926).

[103] Ellis, C., *Chem. Met. Eng.*, 16, 1928; for the use of a sun lamp in testing the durability of color in brightly colored urea resins, see Houwink, R., *Trans. Inst. Plastics Ind.*, **5,** No. 9, 16; *Chem. Abs.*, **30,** 3905 (1936).

[104] Röhm, O., German P. 295,340, June 5, 1915; *J. Soc. Chem. Ind.*, 296 **(1917).**

[105] E. I. du Pont de Nemours & Co., *Ind. Eng. Chem.*, **28,** 1160 (1936); Barrett, H. J., and Strain, D. E., British P. 465,789, May 14, 1937; *Chem. Abs.*, **31,** 7444 (1937); Plauson, H., (Roehm and Haas Co.), U. S. P. 2,086,093, July 6, 1937; *Chem. Abs.*, **31,** 5811 (1937); Chalmers, W., U. S. P. 2,087,468-9, July 20, 1937; *Chem. Abs.*, **31,** 6378 (1937).

[106] Melville, H. W., *Proc. Roy. Soc.*, **A163,** 511 (1937); *Brit. Chem. Abs.*, **1938A,** 261.

[107] Ogawa, W., Hanyu, T., and Yanagihashi, T., *Researches Electrotech. Lab., Tokyo, No. 178,* 78 pp. (1926); *Chem. Abs.* **21,** 659 (1927).

required, Moss and White[108] employ synthetic aniline (or other amine)-furfural resins, adding these to lacquers containing one or more derivatives of cellulose, such as cellulose nitrate, acetate, etc., and a volatile organic solvent, other natural or semi-synthetic resins, plasticizers, pigments or dyes. Phenol or ketone furfural resins also may be used.[109]

Most of a series of synthetic and natural resins and gums studied by Gamble and Stutz[110] tended to decompose in ultraviolet light. This change was accompanied by a yellowing and an increase in the ultraviolet absorption coefficients. Ester gum was classified as being relatively opaque and also relatively stable to these radiations.

In general, the resinous materials are both more opaque and less sensitive to ultraviolet light than are the oleoresinous or nitrocellulose films. Incorporation of a resin therefore affords a certain degree of protection to such sensitive materials. The most desirable type of resin to use would be one which is both opaque and stable to these rays, but there are only a few such resin esters such as Congo, manila and rosin. It is also necessary to consider other factors, such as the physical and chemical properties of the resin and its resistance to weathering. Certain synthetic resins may have a chemical stabilizing action on nitrocellulose even though their own ultraviolet absorption characteristics may be undesirable. The phenol-formaldehyde, glycerol-phthalic anhydride and coumarone-indene types are fairly satisfactory. These all exhibit about the same high opacity, but differ in their sensitivity to the ultraviolet, the coumarone-indene group being the most readily decomposed. In general, the natural gums and resins are both less sensitive and more transparent than are the synthetic materials. Kauri gum was found to be the most stable of the natural resins measured. Vinyl acetate and vinyl chloride have high transparency but are considerably decomposed. A mixture of polymerized vinyl acetate and chloride is both more opaque and less sensitive than vinyl acetate alone.

With a view to obtaining photographic films more transparent than gelatin to the short ultraviolet rays, Dote and Shidei[111] measured the absorption of films from solutions of agar agar and of commercial viscose films. The films were more transparent than the corresponding solutions, which were themselves more transparent than gelatin especially in the extreme ultraviolet.

Minor[112] has employed ultraviolet for bleaching rosin. On the other hand, coumarone resin[113] is darkened on exposure to an ultraviolet lamp for three hours at a distance of a few inches.

The solubility of colored resinates submitted to the action of light has been investigated by des Bancels.[114] Colored resinates were prepared by treating resin with aqueous solutions of alkali hydroxides, adding a suitable coloring matter (safranine, rhodamine, etc.) and then precipitating with a salt of zinc or magnesium. These resinous substances, when dissolved in a volatile solvent, spread in a thin layer on glass plates, dried and exposed to a mercury-vapor lamp, became,

[108] Moss, W. H., and White, B. B., British P. 307,290, 1928, to British Celanese, Ltd.; *Chem. Abs.*, **23,** 5338 (1929).

[109] Moss, W. H., and White, B. B., British P. 307,291, 307,289, 1928, to British Celanese, Ltd.; *Brit. Chem. Abs.*, **B,** 469 (1930).

[110] Gamble, D. L., and Stutz, G. F. A., *Ind. Eng. Chem.*, **21,** 330 (1929).

[111] Dote, S., and Shidei, T., *Japan J. Physics*, **5,** 157 (1929); *Brit. Chem. Abs.*, **A,** 661 (1930).

[112] Minor, L. C., U. S. P. 939,733, Nov. 9, 1909; *Chem. Abs.*, **4,** 521 (1910).

[113] Ellis, C., and Rabinovitz, L., *J. Ind. Eng. Chem.*, **8,** 800 (1916).

[114] des Bancels, L., *Compt. rend.*, **155,** 280 (1912); *J. Chem. Soc.*, **102** (II), 882 (1912).

at the end of a certain time, insoluble in such solvents as benzene, but soluble in methyl or ethyl alcohol.

According to Chinchin,[115] the action of sun and electric rays on rosin causes the formation of a more stable form, insoluble in petroleum ether, having a different dielectric constant and resulting in a molecular agglomeration.[116]

The colloidal condition of stearates, palmitates and oleates of copper, aluminum, zinc, calcium and other water-insoluble soaps is affected adversely and their solubility is impaired by ultraviolet irradiation.[117]

Varnishes and Lacquers

Wolff[118] believed the shrivelling observed to occur in varnishes dried in red light due to a slight retardation by the rays of the surface oxidation, and a greater retardation of polymerization in the inner layers. In light of shorter wave-lengths the processes were thought to proceed at nearly equal rates. Vollmann[119] believes the red rays cause an unequal distribution of heat which influences polymerization in the inner layers.

In the laboratory of the senior author, a large number of samples of varnishes of various grades have been exposed to ultraviolet rays. The behavior of varnishes varies greatly, depending on the composition. Some samples are bleached, others are darkened and still others are very little altered in color.

In the application and treatment of varnish, Clover[120] conveys the varnished articles through a chamber exposed to heat and to light rich in ultraviolet rays.

Ultraviolet accelerated weathering tests have been extensively used for varnishes, lacquers and enamels. Mougey[121] was unable to find a direct relationship between the results of these and of service tests when different types of materials were compared. In early tests made by Mougey on black baking fender enamel, panels failed on the test rack before they did under direct ultraviolet irradiation. When the panels were soaked in water over night and exposed to the ultraviolet during the day, they failed in a few days, but the results were of no value unless care was taken to remove surface water. Failure occurred in a few minutes at the areas where surface water lay on the panels. Finishing varnishes subjected to this test usually failed in one cycle, with no relation between the results of the test and the durability of the varnish. It was apparent that this test favored hard-drying finishes. A rotating wheel type of apparatus was used, half immersed in water and rotating at a rate of two revolutions per hour under the ultraviolet lamp. In this way the panels supported on the wheel were given time for drainage and evaporation of surface moisture and then exposed. A Duco nitrocellulose enamel which withstood exposure on the roof test rack for over two years failed in two days in this test. A finishing varnish with a life of three months on the

[115] Chinchin, I., *Bumazhnaia Promyshlenost, No. 12* (1924); *Chem. Abs.*, **19**, 2273 (1925).

[116] For extinction coefficients of crude and bleached Japan wax, see Sakuma, I., and Momose, I., *J. Soc. Chem. Ind. Japan*, **38**, 218 (1935); *Chem. Abs.*, **29**, 5296 (1935). Crude wax showed a remarkable absorption at 6600A. Sunlight bleaching is facilitated by extraction of the pigment with alcohol. Sakuma, I., Momose, I., and Shomura, J., *J. Soc. Chem. Ind. Japan*, **40**, 48 (1937); *Chem. Abs.*, **31**, 6042 (1937); Sakuma, I., and Momose, I., *J. Soc. Chem. Ind. Japan*, **40**, 170 (1937); *Chem. Abs.*, **31**, 6495 (1937).

[117] Jones, H. I., *Chem. Met. Eng.*, **28**, 489 (1923); *J. Soc. Chem. Ind.*, **42**, 410A (1923).

[118] Wolff, H., *Farben Ztg.*, **24**, 1119, 1389 (1919); *J. Chem. Soc.*, **115**, 915A; see, however, Ragg, M., *Farben Ztg.*, **24**, 1308 (1919).

[119] Vollmann, H., *Farben Ztg.*, **24**, 1427 (1919).

[120] Clover, G. R., U. S. P. 1,646,010, Oct. 18, 1927; *Brit. Chem. Abs.*, **B**, 916 (1927).

[121] Mougey, H. C., *Ind. Eng. Chem.*, **17**, 412 (1925); see also Jenkins, L. D., and Croll, P. R., *Ibid.*, **19**, 1356 (1927).

roof test would stand two or three weeks on the wheel. Apparently, there was no connection between the results of the test and the life of finishing materials on the roof test rack. The results were better when the wheel was continuously rotated day and night and the lamp used only during the day.

Wolff and Zeidler[122] prepared test films of the coating material on a colored gelatin film glued on paper strips. When dry, the film was placed with the coated side on a glass plate, and the gelatin removed with water at 50°C. It is then tested for tensile strength, elasticity and elongation. A kauri varnish film after exposure to the light of a quartz lamp showed an increased extension velocity.

Hansen[123] described a very simple and comparatively inexpensive test in which panels 2.5×13 cm. are exposed in a shallow pan under a source of ultraviolet light. By means of an intermittent siphoning apparatus, the panels are periodically covered with water and allowed to dry out. A cycle of one and one-half hours dry and one-half hour wet exposure was used, but the method when published had not yet been standardized with materials of known characteristics. Tognoni and Trolliet report favorable results with the Weather-Ometer.[124]

von Mühlendahl and Schulz[125] rotate a vertical wheel partly immersed in water, once in fifteen minutes. One day in this test is said to produce results closely paralleling one month of weathering.[126]

An embrittling test for predicting the durability of varnishes was devised by Wilson.[127] In it, varnish films on metal strips are exposed to a carbon arc or to Mazda lamps at a distance of 15 inches until they are so affected that they crack or whiten on bending double at 0 or 22°C. over a 3 mm. rod. The time of exposure to light required to produce this effect is taken as a measure of durability. Levy[128] found that this test, although valuable for classifying good and poor grade varnishes, would not rapidly distinguish grades of the newer types of synthetic resin coatings. An improvement by which the coatings are applied to surfaces of rubber sheeting that can be stretched instead of bent is suggested to make observation easier. Snitter[129] used a flexometer in which the test panel is gradually bent, the line at which bending is effected being observed under a magnifying glass. The angle at which fissuring of the varnish film occurs is noted. He did not find that artificial aging methods give results comparable to the effects of exposure to the weather.[130]

Nitrocellulose Lacquers. Particular attention has been devoted to the light-stability of the newer types of coatings. Stutz[131] made ultraviolet absorption studies of lacquer films, noting particularly the effects of the addition of plasticizers and gums. In general, the light penetrates some distance into the film before being completely absorbed. Similar data on films of acetylcellulose, both pure and plasticized with tritolyl phosphate and *p*-toluenesulfonanilide have been

[122] Wolff, H., and Zeidler, G., *Farben Ztg.*, **32**, 2135, 2708 (1927); *Chem. Abs.*, **22**, 1860 (1928).

[123] Hansen, H. V., *Ind. Eng. Chem.*, **20**, 1384 (1928).

[124] Tognoni, C. A., and Trolliet, A. L., *Chimie & Industrie*, **38**, 647 (1937); *Chem. Abs.*, **32**, 3642 (1938).

[125] von Mühlendahl, E., and Schulz, H., *Z. angew. Chem.*, **40**, 1185 (1927).

[126] For a description of a wheel developed by the Ditzler Co., see Denham, A. F., *Automotive Industries*, April 9, 1927.

[127] Wilson, J. H., *Bureau Standards J. Research*, **7**, 73 (1931).

[128] Levy, S. A., *Am. Paint Varnish Mfrs. Assoc. Circular 410*, 146 (1932); *Chem. Abs.*, **26**, 3939 (1932).

[129] Snitter, P., *Bull. inst. pins*, 223 (**1933**); *Chem. Abs.*, **28**, 1554 (1934).

[130] See also Martin, R. C., *Metal Cleaning and Finishing*, **6**, 561 (1934).

[131] Stutz, G. F. A., *Ind. Eng. Chem.*, **18**, 1235 (1926).

given by Orlova.[132] Data are reported by Nakashima and Negishi[133] for various cellulose films as altered by swelling and softening agents.

The viscosity of nitrocellulose solutions decreases on exposure to light.[134] The colloidal changes occurring in nitrocellulose collodion with time and under the influence of ultraviolet light have been studied by Breguet[135] by fractional precipitation of the nitrocellulose by the method of Duclaux and Wollmann, using benzene instead of water to prevent precipitation of the camphor. The weight, viscosity and nitrogen content of the various fractions was determined. The results were interpreted in terms of the Duclaux theory of the constitution of reversible gels as follows: In a collodion the most complex nitrocellulose molecules have the greatest tendency to polymerize and swell, and in a nitrocellulose solution the solid phase is formed of the largest granules, the cells of which are filled with a dispersion of the finer granules of the solvent. The granules of collodion are in equilibrium with the solvent, and in time the cohesion forces of the molecules in the granules gradually diminish, and the granules are progressively depolymerized with resulting decrease in swelling, made evident by decreased viscosity. This aging does not proceed indefinitely but tends to a limit which depends on the concentration, temperature, and nature of the nitrocellulose collodion. Aging is accelerated by heat, light and mechanical treatment. The changes taking place in collodion with time are thus due to its changing from an emulsoid to a suspensoid. The general effects of ultraviolet light on celluloid or collodion are to lower the viscosities of all fractions and to decrease the total yield of high-viscosity nitrocellulose and correspondingly increase the yield of low-viscosity nitrocellulose.

Branchen and Prachel[136] proposed to make practical application of the ability of ultraviolet light to reduce the viscosity of an acetone solution of cellulose acetate in the presence of a fatty acid, preferably formic or acetic. In fifty hours a viscosity ranging from one-half to one-fifteenth that of the original value may be obtained.

During degradation by ultraviolet rays the tensile strength of cellulose acetate films with the same acetyl numbers varies as the viscosity. The stretch varies similarly but to a greater degree.[137] During this form of aging of a film base, there is associated with the depolymerization of the ester (shown by the decrease in viscosity) an increase in brittleness and a yellowing.[138]

When employed in layers in safety glass, nitrocellulose has been found to be light-sensitive, decomposing on prolonged exposure to light. Cellulose acetate promised better results as it is more stable, but it is still not ideal for the intermediate layer.[139]

It has been claimed that the instability toward light of nitrocellulose films depends on impurities introduced during preparation.[140] The most harmful impurities are ferrous salts, ferric salts being less so. Extraction of the nitrocellulose with hydrochloric acid can remove most of the iron salts. Decomposition products of cellulose, organic acids, aldehydes and sodium hypochlorite used for bleaching have no effect, but copper salts are also harmful. The photochemical stability is independent of the temperature of nitration and the thermal stability.

Callahan[141] stated that a clear film of cellulose nitrate exposed to the ultraviolet rays of the sun's spectrum for only a few days becomes so brittle that it will not stand bending without cracking. The use of oils and plasticizers will extend this life but eventually failure will occur. However, if such a film is protected from the sun's rays by the use of opaque pigments, particularly when the film is applied to a rigid surface such as steel, almost indefinite resistance to sunlight will result. Scheiber[142] attributes the brittleness produced by light to the possibility of crystallization of the cellulose esters. In the absence of pigment, plasticizer and resin, ultraviolet light causes in nitrocellulose films a yellowing when wetted by 10-per cent sodium hydroxide, an increase in the wettability by water and ethyl acetate, an acid reaction and an unpleasant odor. The changes may be the result of saponification following the production of free organic acids.[143] Kraus[144] believes that the degree of yellowing in nitrocellulose lacquers depends on the nature and concentration of the plasticizer as well as on the exposure.[145]

It has been found[146] that the absolute intensity of yellowing of nitrocellulose films with 33.3 per cent tritolyl phosphate as plasticizer, when exposed to a mercury arc, was greater for 135μ films than for 15μ films. But when expressed as amount of yellowing per unit thickness, the change was greater in the thinner films. The amount of additional yellowing decreases for each added increment of time.

Kraus[147] finds that ultraviolet greatly impairs the plasticity imparted to nitrocellulose by butyl oleate or benzyl stearate. Palatinol AS and Palatinol L are superior. Irradiation caused strong yellowing with Toplast, somewhat less with benzyl stearate and very little with Palatinol AS, Palatinol L and butyl oleate.

Nishizawa[148] follows the rate of decomposition of nitrocellulose by light by determining nitrogen dioxide with α-naphthylamine. Kraus, however, did not believe the destruction of the film to be simply related to either the degree of denitration or to the loss of the solubility in acetone. Although the ability of the plasticizers to combine with the nitrogen decomposition products had an influence on the characteristics, direct relations could not be discerned.

Attempts have been made to increase the stability of nitrocellulose films to sunlight, *i.e.*, to decrease their chalking, by the introduction of pigments. McKim[149] prepared a clear cotton solution and in this ground a small amount of zinc oxide to determine whether a pigment opaque to ultraviolet light exerted a protective

[132] Orlova, O. V., *J. Tech. Physics, U.S.S.R.*, **4**, 1170 (1934); *Chem. Abs.*, **29**, 8321 (1935).

[133] Nakashima, T., and Negishi, M., *J. Soc. Chem. Ind. Japan*, **39**, Suppl. binding, 102, 104 (1936); *Chem. Abs.*, **30**, 5407 (1936).

[134] McBain, J. W., Harvey, C. E., and Smith, L. E., *J. Phys. Chem.*, **30**, 312 (1926); *Chem. Abs.*, **20**, 1741 (1926).

[135] Breguet, A., *Rev. gen. colloides*, **3**, 200, 230 (1925); *Chem. Abs.*, **19**, 3590 (1925). See also Rogovin, Z. A., and Glazman, S., *J. Gen. Chem. (U.S.S.R.)*, **8**, 498 (1938); *Chem. Abs.*, **32**, 7260 (1938).

[136] Branchen, L. E., and Prachel, C. U., U. S. P. 1,658,368, Feb. 7, 1928, to Eastman Kodak Co.; *Chem. Abs.*, **22**, 1237 (1928).

[137] Grard, J., *Bull. soc. chim.*, **53**, 1308 (1933); *Chem. Abs.*, **28**, 4222 (1934).

[138] Kozlov, P. V., and Zueva, R. V., *Photo-Kino Chem. Ind. (U.S.S.R.)*, No. 5, 14, 1935; *Chem. Abs.*, **30**, 4107 (1936).

[139] Ellis, C., *Chem. Met. Eng.*, 16 (1928).

[140] Mindlin, S. S., Zel'dovich, P. Y., Kaplan, M. Y., Kuz'mina, L. I., and Remennikova, V. S., *Plasticheskie Massui*, No. 4, 4, 1934; *Chem. Abs.*, **29**, 3154 (1935).

[141] Callahan, M. J., *Chem. & Industry*, **47**, 34, 236T (1928).

[142] Scheiber, J., *Farbe und Lack*, 190 (**1928**); *Chem. Abs.*, **22**, 3054 (1928).

[143] Beutel, E., and Kutzelnigg, A., *Farbe und Lack*, 351 (1934); *Brit. Chem. Abs.*, **B**, 804 (1934); see also Gloor, W. E., *Ind. Eng. Chem.*, **23**, 980 (1931).

[144] Kraus, A., *Paint Varnish Production Mfr.*, **13**, 16, 18 (1935); *Chem. Abs.*, **30**, 307 (1936); *Farbe und Lack*, 545, 556 (1935); *Chem. Abs.*, **28**, 891 (1934).

[145] A general discussion of the aging of oil, gum, resin and cellulose derivatives under the influence of light and air and of the effects of pigments upon it has been given by Nauroy, A., *14 Congr. chim. ind. Paris* (Oct. 1934); *Chem. Abs.*, **29**, 6443 (1935). Note also Rosenthal, L., and Schultze, G., *Farben-Chem.*, 53 (Feb., 1934); *Synthetic and Applied Finishes*, 65 (June, 1934).

[146] Communication III from the Untersuchungs-und Forschungs Laboratorium für Lacke und Farben, Berlin, *Farben-Ztg.*, **42**, 667 (1937); *Chem. Abs.*, **31**, 8960 (1937); Wolff, H., and Zeidler, G., *Paint Varnish Production Mfr.*, **17**, 7, 10 (Sept., 1938); *Chem. Abs.*, **32**, 7162 (1938).

[147] Kraus, A., *Farbe und Lack*, 269 (1938); *Chem. Abs.*, **32**, 8806 (1938).

[148] Nishizawa, Y., *J. Chem. Soc. Japan*, **50**, 258, 327, 391 (1929); *Chem. Abs.*, **25**, 5627 (1931).

[149] McKim, W. A., *Ind. Eng. Chem.*, **18**, 1239 (1926); de Waele, A., *J. Soc. Dyers Colourists*, **43**, 42 (1927).

action. The reduction in distensibility produced by an ultraviolet exposure, which in the clear film caused a destruction of 100 per cent, was in this way reduced to but 60 per cent. The breaking strength of the clear film increased from 9 to 18 units and in the pigmented film from 30 to 36.

For the protection of automobile finishes, Denham[150] found a fairly large amount of pigment necessary. Although opaque colors in general stood up better than those of lower opacity, some, notably the Para toners, did not furnish as much protection. Although more opaque than madder lakes, they made up into less durable lacquers. White pigments (titanium, lithopone, zinc oxide) are very durable but zinc sulfide is undesirable, since it turns brown on exposure. Ultramarine lacks durability, since it does not provide protection against actinic rays. Of true lake colors, alizarin pigments produce the most durable so-called lake colors in pyroxylin lacquers. Since they have poor covering qualities, they must be strengthened with other materials which detract from durability.

In discussing accelerated weathering of lacquer enamels, Nelson[151] noted that it is possible to produce such failures as hair-line checking by increasing the oxygen content of the air in the light-exposure chamber and by including periodic exposure to humid air containing sulfur dioxide and carbon dioxide. He believed the relative ratings of a series of nitrocellulose lacquers in this test agreed reasonably well with outdoor exposure ratings.

Pigmented enamels made with cottons of higher viscosity showed greater durability and greater tensile strength and distensibility than those made with 0.5-second cotton. This may be due to the longer fibers used in the production of the cottons of higher viscosity, or to the freedom from suspended matter usually present in the solutions of the latter. Greater durability resulted from a ternary mixture containing 50 per cent of 0.5-second cotton, 24 per cent of 4-second cotton and 26 per cent of leather dope. The last by itself showed the poorest durability of all the cottons tested.

In weathering, light-colored enamels containing 19.5 per cent of 0.5-second cotton yellowed more than those containing 16 per cent of the same cotton; the former, containing pigment transparent to ultraviolet light, were more durable than the latter, but with pigments opaque to ultraviolet light, the enamels containing the lower cotton content were the more durable. Increasing the gum content from 1.5 to 3 per cent decreased durability and increased gloss when dammar gum was used, but with ester gum both these properties were increased. Comparative tests of tricresyl phosphate and triphenyl phosphate showed little preference except when the tests were run at 48°C., when the films containing the latter rapidly became weak and brittle, apparently as a result of crystallization of the plasticizer. The addition of clear lacquer to a pigmented lacquer in the finishing coats, or a finishing coat of clear lacquer or of varnish, always decreased the durability of the pigmented lacquer job. A wax finish stands up better than a buff finish.

Von Mühlendahl and Schulz[152] studied the influence of plasticizers on nitrocellulose under the influence of light and heat, judging it from the color of a mixture of equal amounts of the two products when heated to 100°C. or exposed to the rays of a quartz lamp.

According to Merz,[153] weathering under a carbon arc, and the results of a baking-bending test of a series of red, white and black lacquers with varying quantities of ester gum, gave the best correlation with outside weathering.

[150] Denham, A. F., *Automotive Industries*, **56**, 544 (1927).
[151] Nelson, H. A., *Can. Chem. Met.*, **10**, 11 (1926); *Chem. Abs.*, **20**, 995 (1926).
[152] Von Mühlendahl, E., and Schulz, H., *Farbe und Lack.* 276 (1927); *Chem. Abs.*, **22**, 3055 (1928).
[153] Merz, O., *Farben Ztg.*, **36**, 316, 362 (1930); *Chem. Abs.*, **25**, 608 (1930).

Studies of the ultraviolet light absorption by lacquer films and their constituents indicated that within the range present in sunlight, all of the absorption by an ordinary lacquer is due to ester gum with lesser absorption by such plasticizers as tricresyl phosphate and castor oil.[154] The failure of ordinary lacquer films is ascribed to excited ester gum molecules transferring their energy to neighboring nitrocellulose molecules. Avoidance of the use of ingredients opaque to the ultraviolet of sunlight should improve the light resistance. In general agreement with this, Münzinger[155] observed that nitrocellulose films containing 29 different softeners were all more sensitive than the nitrocellulose alone. Castor oil and tritolyl phosphate caused the greatest and glycol monomethylphthalate the least alteration on exposure. Münzinger also tabulated the changes in fluorescence colors resulting from the exposure.

The Elektrizitätswerk Lonza[156] produces a varnish containing diphenylamine to retard the absorption of ultraviolet light by nitrocellulose films.

Dykstra[157] uses crotyl cellulose or allyl cellulose and a drier, such as cobalt oleate, for lacquers which may be baked. Ultraviolet light may be used for insolubilizing the films of crotyl cellulose. Ethylcellulose films approximate acetylcellulose films in transparency and light resistance. Prolonged exposure of ethylcellulose films to ultraviolet light at high temperatures depolymerizes the cellulose molecule with lowering of the viscosity.[158]

Since the cellulose acetate lacquers are more resistant to light than cellulose nitrate lacquers, it has been proposed to coat the latter with the former.[159] However, cellulose acetate does not absorb the rays which decompose the nitrate in the lower layers so that such protection is not complete. To overcome this, many additions to the cellulose acetate layer have been suggested to render them opaque. The addition of 7 oz. of stannic acid per gallon has been proposed for use in protective coatings for airplane wings by Doerflinger. In the preparation of an actinism-proof cellulose ester composition, Clewell[160] coats transparent sheets of pyroxylin on both sides with a colorless transparent oil-resin varnish, *e.g.*, a copal-linseed oil mixture impervious to ultraviolet light.

In the cellulose acetate of other overcoatings, Staud and Murray[161] use about 2 per cent of phthalic acid neutral esters of monoethers of hydroquinone and their homologs. In the production of laminated glass, two layers of overcoating are placed on each side of the cellulose nitrate film which is then incorporated between two sheets of glass. (It was also claimed that crystallization within the cellulose ester sheets produced beautiful effects and that such materials might be useful in the manufacture of toilet articles, novelties, etc.)

Many other organic substances have been proposed for this purpose, including polycyclic hydrocarbons or their derivatives, such as phenanthrene, naphthalene,

[154] Davey, W. P., Duncan, D. C., and Wiggam, D. R., *Phys. Rev.*, **35**, 1423 (1930); *Ind. Eng. Chem.*, **23**, 904 (1931).
[155] Münzinger, W. M., *Chem. Ztg.*, **56**, 851 (1932).
[156] Swiss P. 128,476, May 25, 1927, to Elektrizitätswerk Lonza; *Chem. Abs.*, **23**, 2840 (1929).
[157] Dykstra, H. B., U. S. P. 1,920,297, Aug. 1, 1933; *Chem. Abs.*, **27**, 4943 (1933).
[158] Ushakov, S. N., Shneer, I. M., Demina, E. N., and Ijboldina, *Rev. gén. mat. plastiques*, **13**, 341 (1937); *Chem. Abs.*, **32**, 3603 (1938).
[159] Application of Steel, P. C., U. S. Serial No. 425, 353. Cited by Staud, C. J., and Murray, T. F., Jr., U. S. P. 1,950,907.
[160] Clewell, J. H., Jr., U. S. P. 1,647,435, Nov. 1, 1927, to E. I. du Pont de Nemours & Co.; *Chem. Abs.*, **22**, 317 (1928).
[161] Staud, C. J., and Murray, T. F., U. S. P. 1,950,907, March 13, 1934; *Brit. Chem. Abs.*, **B**, 161 (1935).

chloronaphthalene, anthracene or *p*-amino-benzoic acid, phthalimide, nitroanisole, nitrobenzene, quinaldine, benzyl benzoate, glycerol butyl phthalate and β-methoxy-methyl phthalate, dibenzofuran, diphenylbenzene, diphenylguanidine, xanthydrol or phthalanil.[162]

Vanadium, cerium or titanium salts of a half ester of phthalic acid,[163] as well as triphenyl compounds of antimony or bismuth have also been suggested for this purpose.[164] Dreyfus [165] used a topcoat of phenol-furfural resin. This resin film is dried and converted to the insoluble, infusible state by baking, exposure to sunlight or ultraviolet light. Bradshaw [166] incorporates an iron or cobalt salt of naphthenic acid or a resin acid. Organic or inorganic compounds of copper may be added to purified benzylcellulose used as a basis for transparent films, sheets or plastics to render them resistant to the action of light and heat.[167]

According to Cofman and de Vore,[168] the wave-length most effective per quantum absorbed in causing the acid decomposition of nitrocellulose is about 3100A. It was to prevent the passage of this wave-length that most of the materials listed above were introduced. The observation by Rayleigh that celluloid containing malachite green becomes red when exposed to sunlight may be explained as due to the action of the liberated nitrogen oxides on the dye. Trevy [169] finds the light-yellowing of celluloid films most intense under wave-lengths between 3000 and 3500A.[170] Traces of metals may increase the yellowing. Durophen lacquer 218 V of the firm of Kurt Albert is completely opaque to ultraviolet light of wave-lengths shorter than 4000A even in thin layers. In the visible range, it transmits light increasingly toward the red end of the spectrum.[171]

[162] British P. 371,901, Oct. 24, 1930, to Eastman Kodak Co.; *Chem. Abs.*, **27,** 3094 (1933); Staud, C. J., U. S. P. 1,958,683; *Chem. Abs.*, **28,** 4614 (1934); Murray, T. F., U. S. P. 1,958,711; *Chem. Abs.*, **28,** 4615 (1934); U. S. P. 1,976,359; *Chem. Abs.*, **28,** 7562 (1934); Canadian P. 339,837, March 6, 1934; U. S. Patent 2,043,805; Richardson, E., and Staud, C. J., U. S. P. 1,958,714-5; *British Chem. Abs.*, **B,** 278 (1935); U. S. P. 2,017,165; *Brit. Chem. Abs.*, **B,** 1109 (1936); Staud, C. J., and Murray, T. F., U. S. P., 1,994,596; *Chem. Abs.*, **29,** 3182 (1935); Kocher, N. S., U. S. P., 1,973,488; *Chem. Abs.*, **28,** 7043 (1934).

[163] Salzberg, P., U. S. P. 1,965,608; Canadian P. 333,043, June 6, 1933; *Chem. Abs.*, **27,** 4428 (1933).

[164] Murray, T. F., U. S. P. 1,969,473; *Chem. Abs.*, **28,** 6329 (1934).

[165] Dreyfus, C., U. S. P. 1,964,039, June 26, 1934; *Brit. Chem. Abs.*, **B,** 402 (1935).

[166] Bradshaw, H., U. S. P. 1,962,132; *Chem. Abs.*, **28,** 4904 (1934).

[167] French P. 795,880, March 24, 1936, to Soc. des usines chimiques Rhone-Poulenc; *Chem. Abs.*, **30,** 5690 (1936).

[168] Cofman, V., and de Vore, H. B., *Nature,* **123,** 87 (1929).

[169] Trevy, P., *Rev. gen. mat. plast.*, **13,** 60, 131 (1937); *Brit. Chem. Abs.*, **B,** 767 (1937).

[170] See also Report of Paint and Varnish Research Lab., Berlin, *Farben Ztg.*, **42,** 667 (1937); *Brit. Chem. Abs.*, **B,** 1088 (1937).

[171] Heyne, G., and Schön, M., *Angew. Chem.*, **49,** 784 (1936); *Chem. Abs.*, **31,** 321 (1937).

Chapter 31

Rubber

The absorption of ultraviolet radiations by rubber dissolved in pure hexahydrotoluene has been studied by Scheibe and Pummerer.[1] (See Figure 127.) Of samples of rubber from latex treated with alkali, rubber from non-coagulated latex, and "sol-rubber," the curves of the latter were believed most closely to approximate the absorption of rubber hydrocarbon. Gutta-percha gave a curve of similar type. Kröger and Staude [2] found that isoprene and various samples of rubber exhibit only continuous absorption. Synthetic rubber made from isoprene is more transparent than isoprene itself in the same thickness. The transparency of both synthetic and natural rubber increases with stretching,[3] presumably on account of some molecular change. Rubber vulcanized with sulfur chloride is much less transparent.[4]

Polymerization and Depolymerization

Deresinized, colorless gutta-percha on exposure to ultraviolet light becomes more opaque and brittle, although still completely soluble in benzene.[5] This change has been assumed to be due to a transformation into a crystalline form, the existence of which has been demonstrated microscopically. Kirchhof [6] states that experiments by Porritt [7] indicated that a benzene solution of rubber slowly changes to a gel on exposure to ultraviolet light. Kirchhof found that this could be observed only in a very small volume of solution. With larger volumes, depolymerization apparently occurred with a lowering of the viscosity. There have been many subsequent observations of the reduction of the viscosity of rubber sols by ultraviolet light.[8]

During this alteration of the viscosity of crude rubber solutions, the molecular polarization is not markedly affected, according to Kambara.[9] Garner [10] found that the reduction in viscosity during irradiation occurred particularly in solutions from which oxygen was excluded. On evaporation, there was obtained a depolymerized rubber which readily absorbed oxygen. Ordinarily, however, light and air cause both an oxidation and an increase in tackiness as judged by changes in viscosity. Garner concluded that the effect of light is partly polymerization and partly depolymerization. The latter predominates in an ordinary atmosphere. In nitrogen with but little oxygen, the rubber is in part rendered insoluble. The relative effects of various antioxidants in retarding the decrease in viscosity of irradiated

[1] Scheibe, G., and Pummerer, R., *Ber.*, **60,** 2163 (1927).

[2] Kröger, M., and Staude, H., *Gummi-Ztg.*, **43,** 22 (1928); *Chem. Abs.*, **23,** 306 (1929).

[3] For x-ray data on crystals in stretched rubber, see Clark, G. L., *Ind. Eng. Chem.*, **18,** 1131 (1926).

[4] For the Raman spectrum of rubber, see Gehman, S. D., *J. Am. Chem. Soc.*, **57,** 1382 (1935).

[5] Kirchhof, F., *Kautschuk,* **4,** 254 (1928); *Chem. Abs.*, **23,** 1525 (1929).

[6] Kirchhof, F., *Kautschuk,* 28, 1927; *Chem. Abs.*, **21,** 1377 (1927).

[7] Porritt, B. D., *India Rubber J.*, **60,** 1159 (1920); *Chem. Abs.*, **15,** 1230 (1921).

[8] Gallay, W., *Canadian J. Res.*, **7,** 671 (1932); *Chem. Abs.*, **27,** 1561 (1933). See, however, Dogadkin, B., and Lavrenenko, M., *Kautschuk,* **9,** 97 (1933); *Chem. Abs.*, **27,** 4953 (1933).

[9] Kambara, S., *J. Soc. Chem. Ind. Japan,* **39,** 138 (1936); *Chem. Abs.*, **30,** 6298 (1936).

[10] Garner, T. L., *Trans. Inst. Rubber Ind.*, **4,** 413 (1929); *Brit. Chem. Abs.*, **B,** 445 (1929).

rubber stands in no simple relation to their effects on actual oxidation. By favoring the formation of an insoluble polymer on the surface of exposed rubber, antioxidants may, indeed, accelerate the loss of surface tackiness.

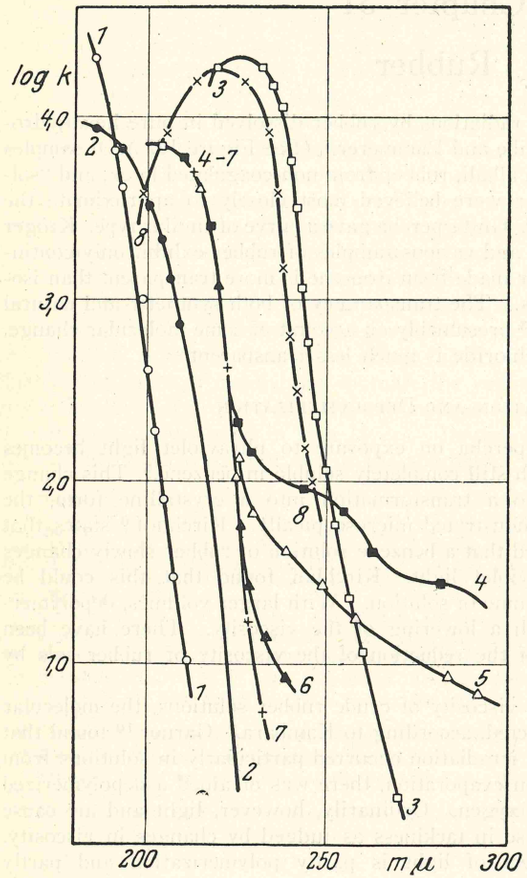


FIGURE 127.

Absorption of Latex, Sol-Rubber and Related Compounds (Scheibe and Pummerer, *Berichte der deutschen Chemischen Gesellschaft*).

1. Diallyl
2. Trimethylethylene
3. Dimethylbutadiene
4. Latex purified with NaOH and coagulated
5. Latex, uncoagulated
6. Latex, purified with NaOH
7. Sol rubber
8. Isoprene

Mojen[11] found that no change in the viscosity of ordinary rubber solutions containing monochloracetic acid occurs in light when oxygen is rigorously excluded. The same was true also of balata solutions containing acetic acid or its chlorine substitution products. But with oxygen present, the rubber sols changed to an insoluble product even in darkness. The protective power of the natural antioxidants, which are probably basic, is destroyed when they are combined with acids. A benzene solution of purified gutta-percha irradiated in an atmosphere of hydrogen gave on evaporation a white, unctuous, fragile product which melted to a limpid oil at 90°C. On cooling, the latter gave a tough product like the original gutta-percha, so that heating was assumed to have destroyed the crystalline structure. The melting point of the microcrystals of the irradiated material was believed to be lower than that of the crystals which are obtained in films formed by evaporation of nonirradiated solutions. The product left after the evaporation of the benzene from an irradiated solution redissolved to a clear solution in benzene, if the irradiation is conducted in hydrogen; but irradiation of a film with air present gives a product which is partly insoluble. Such effects are not observed in the case of rubber. The different behavior of gutta-percha is ascribed to its higher state of polymerization.

[11] Mojen, H. P., *Kautschuk*, **13**, 39 (1937); *Chem. Abs.*, **31**, 5214 (1937).

No change in the unsaturation of a 1-per cent solution of pale crepe rubber can be detected by a modified Wijs method after irradiation under carbon dioxide in a quartz flask for 28 to 45 hours by a quartz mercury-vapor arc.[12]

The ultraviolet radiations present in sunlight tend to polymerize rubber, isoprene and styrene, especially in the presence of sensitizers (compare the cinnamic acids, Chapter 25).[13] Ether solutions of rubber under nitrogen in sealed tubes generally gelatinize when exposed to sunlight, but the length of time required, sometimes weeks, varies so greatly that this is not a practicable method of bringing about gelation. The light rubber obtained by evaporating the ether gel is entirely insoluble in ether if the illumination has been sufficiently prolonged. On milling rolls, it gradually becomes ether-soluble again, but it differs from gel rubber in that the addition of diethylamine, piperidine, etc. does not make it ether-soluble. Its iodine number is 94 to 98 per cent of that of the original sol rubber. Apparently the chemical effect of the irradiation is a polymerization involving only from 2 to 6 per cent of the double bonds. The gelation can be regulated and reproduced at will by the use of various sensitizers containing a carbonyl group. With eosin, gelation can be demonstrated in about ten minutes in quartz under a mercury arc, and even 0.2 per cent solutions of rubber in carbon tetrachloride can be made to gel. It is the longer wave-lengths between 2800 and 3150A which are believed effective. Methylene blue and malachite green offered no advantages over eosin. Diphenylketone (3150 to 4000A) and benzanthrone (3150 to 4200A) are also effective. Benzaldehyde also produces gelation, but with it and with acetaldehyde the conditions do not seem as simple as with the ketones. Methylbenzyl oxide proved to be moderately effective, but aliphatic esters and such colored hydrocarbons as perylene had no action. The same sensitizers also bring about the gelation of liquid isoprene and isoprene emulsions in soap solutions in glass. The resulting isoprene rubbers give iodine numbers of 94 to 99 per cent of the theoretical, but with evolution of considerable quantities of hydrogen iodide.

Liquid styrene is readily polymerized to solid styrene resin in glass in the presence of sensitizers in several days of exposure to a 200-watt lamp at room temperature. In the presence of diphenyl ketone or benzanthrone at 60-70°C. and with a 500-watt lamp, the change is complete in a few hours. The reaction proceeds two to three times as rapidly under cylinder nitrogen containing some oxygen as it does under pure nitrogen. Since it is oxygen in the gas phase that is effective, it may be assumed that gelation begins at the gas-liquid interface. Such antioxidants as hydroquinone inhibit the reaction. The presence of "active oxygen" during the irradiation of diphenyl ketone, phenylmethyl ketone and even of diethyl ketone was shown by means of a benzidine-sodium chloride solution. Iron compounds (ferric chloride, ferric acetylacetonate, iron pentacarbonyl) do not accelerate the photogelation of rubber solutions. Kirchhof[14] also noted that when a

[12] Fisher, H. L., and Gray, A. E., *Ind. Eng. Chem.*, **18**, 414 (1926).
[13] Pummerer, R., and Kehlen, H., *Ber.*, **66B**, 1107 (1933); *Chem. Abs.*, **27**, 6018 (1933).
[14] Kirchhof, F., *Kautschuk*, 28, (1927); *Chem. Abs.*, **21**, 1377 (1927).

benzene solution of phosphorus is added to a rubber solution before exposure, irradiation produces a gel similar to that produced with dilute sulfur chloride. This gel is formed even in rubber solutions which have previously been depolymerized by light. If rubber-phosphorus solution which has been exposed to light but not gelatinized is evaporated and extracted with acetone, the resulting rubber is similar in physical properties to rubber vulcanized with sulfur chloride. Similarly treated samples in which no phosphorus had been added gave only a weak, tacky product. There is no change apparent in phosphorus-containing benzene solutions of rubber exposed in carbon dioxide to daylight at 70-75°C. Without rubber present, benzene solutions of yellow phosphorus deposit red phosphorus on exposure to ultraviolet light or to sunlight, but rubber has a protective action so that in its presence this reaction does not occur. The phosphorus photovulcanization occurring in rubber solutions in ultraviolet light resembles sulfur vulcanization in that gel formation is greatly accelerated by zinc xanthate.

In latex, polymerization by quinone is readily aided by irradiation.[15] At 90°C., air causes depolymerization, even in light. When portions of quinone and latex were irradiated separately and mixed in darkness, no enhanced polymerization resulted. It also does not result from the irradiation of latex alone. The photochemical polymerization is not inhibited by an excess of hydroquinone, but it is greatly reduced by an excess of a dark brown oxidation product of quinone, which may compete in absorbing the effective light. When a solution of rubber in benzene containing quinone is irradiated in the presence of air, there is marked depolymerization at room temperature, but irradiation at −80°C. leads to enhanced polymerization.

The addition of an inorganic cobalt salt or of cobalt resinate to a benzene solution of rubber causes rapid depolymerization, which is accelerated by air and light.[16] The effects of many antioxidants and accelerators upon the development of tackiness in rubber when exposed to a General Electric S-1 lamp have been determined by Blake and Bruce.[17]

Irradiation of chloroprene by the 2537A line leads, after a long induction period, to a polymerization in the condensed phase. A dark polymerization subsequently ensues.[18] Butadiene shows little tendency toward photopolymerization and the quantum yield in the mercury-sensitized reaction is only unity. This compound admixed with methyl methacrylate inhibits the photopolymerization of the latter, which in the absence of this inhibitor has a quantum yield of about one hundred.

No indication of a *cis-trans* transformation by ultraviolet could be found by Meyer and Ferri,[19] although they state that light effects a kind of "vulcanization" by irregular polymerization. When solutions of 1 g. and 2.5 g. of coagulated latex in 100 cc. of cyclohexane were irradiated in a quartz flask in oxygen for ten hours at 5 cm. from a 300-watt quartz mercury arc, elastic gels insoluble in solvents were formed. These were similar to products obtainable by the addition of small amounts of sulfur chloride. Dry gels formed in the absence of oxygen had the mechanical properties of a feebly vulcanized rubber. It is believed that in such gels, the original rubber hydrocarbon chains are oriented in a three-dimensional

[15] Spence, D., and Ferry, J. D., *J. Am. Chem. Soc.*, **59,** 1648 (1937).

[16] Krauz, C., and Franta, I., *Rubber Tech. Conf., London, Preprint No. 13* (May, 1938); *Chem. Abs.*, **32,** 8169 (1938).

[17] Blake, J. T., and Bruce, P. L., *Rubber Tech. Conf., London, Preprint No. 21* (May, 1938); *Chem. Abs.*, **32,** 8833 (1938).

[18] Bolland, J. L., and Melville, H. W., *Rubber Tech. Conf., London, Preprint No. 90,* May, 1938; *Chem. Abs.*, **32,** 8396 (1938).

[19] Meyer, K. H., and Ferri, C., *Helv. Chim. Acta,* **19,** 694 (1936); *Chem. Abs.*, **30,** 6601 (1936); *Rubber Chem. Tech.*, **9,** 570 (1936).

network through the establishment of valence bonds transversely and between the double bonds.

It has been observed that gasoline rubber cements exposed to sunlight in glass in most cases became solvent-thin, although in a few cases gels formed.[20] Carbon tetrachloride cements all formed rigid gels. The behavior of the latter is ascribed to a curing by ultraviolet light and by chlorine resulting from decomposition of the solvent. Similar results were obtained at a slower rate in diffused light. Protection of the gasoline cements by red filters greatly prolonged the time required for them to thin. The higher the rubber content of a cement, the smaller is the change in its viscosity.

Vulcanization

Victor Henri is credited by Helbronner with having used ultraviolet rays as early as 1909-10 for the vulcanization of films made from solutions of rubber. Rubber solutions vulcanized by ultraviolet are stated by Helbronner[21] to be insoluble in the original solvent after they have been dried. Bernstein[22] proposed vulcanizing rubber solutions containing sulfur by exposing them to the action of ultraviolet rays produced by a quartz mercury-vapor lamp, the solutions being spread on a moving metallic ribbon. A solution of rubber in benzene containing 6 per cent of rubber, and sulfur equal to 10 per cent of the rubber, when exposed in a film 0.5 mm. thick required forty to fifty seconds for vulcanization. Ordinary or high temperatures, pressure or vacuum, air or inert gas atmospheres, may be used. Bernstein[23] evaporated a xylene solution of Hevea plantation rubber with 6 per cent of sulfur to a thin film on a transparent quartz plate and covered it with another quartz plate. This was exposed on both sides for forty minutes at a distance of 15 cm. to the rays from a Heraeus lamp of three amperes and 110 volts. The film then possessed the properties of vulcanized rubber and contained 2.56 per cent of combined sulfur. Other experiments showed that the percentage of combined sulfur increased with the time of exposure to the rays. The deterioration of vulcanized rubber on exposure to ultraviolet rays, observed by Henri, is considered to be chiefly due to "after-vulcanization." Stern[24] states that the vulcanization is accompanied by some depolymerization. Ostromuislenski[25] believed that, in the absence of air, the rays activate sulfur by converting it into thiozone. The vulcanization is then affected partly by the latter and partly by the ozone formed simultaneously.[26]

According to Pohle,[27] irradiation of a supersaturated solution of sulfur in rubber, prepared by heating, results in separation of the sulfur. The effect, which is due to the violet and blue rays, can be followed ultramicroscopically by a quartz ultracondenser. The number of particles depends on the intensity of the light and on the time of exposure. Long exposures or high intensities give dense, fine, blue

[20] Novotny, C. K., *Ind. Eng. Chem.*, **26,** 170 (1934).

[21] Helbronner, A., *India Rubber World,* 130 (**1914**); note also *Compt. rend.*, **138,** 1343 (1914); *Chem. Zentralbl.* 326, (**1914**); *Kolloid Z.*, 4, (**1913**); French P. 460,780, July 26, 1913.

[22] Bernstein, G., British P. 17,195, July 26, 1913; U. S. P. 1,240,116, Sept. 11, 1917.

[23] Bernstein, G., *J. Frank. Inst.*, 345, **1913.** Note also Helbronner, A., and Bernstein, G., *Rubber Ind.*, 156 (**1914**); *Caoutchouc et Gutta-Percha,* **12,** 8720 (1915). Green, H., *Ind. Eng. Chem.*, **17,** 802 (1925) has used the ultraviolet microscope in connection with a study of vulcanized latex globules; see also Lucas, F. F., [*Ind. Eng. Chem.*, **30,** 146 (1938)] for observations on untreated latex. Note also Gray, G. W., *Technology Rev.*, **40,** 172, 188, 190, 192 (1938).

[24] Stern, E., *Chem. Ztg., Rep.* 422 (1913).

[25] Ostromuislenski, I. I., *J. Russian Phys. Chem. Soc.*, **47,** 1892-1898 (1915); *J. Soc. Chem. Ind.*, 370 (**1916**).

[26] Meyeringh, D. J., and Wijnand, P. C., British P. 208,167, Dec. 24, 1924; *Chem. Abs.*, **18,** 1589 (1924).

[27] Pohle, H., *Naturwiss.*, **15,** 162 (1927); *Chem. Abs.*, **21,** 1904 (1927).

dispersed fogs and short exposures give a smaller number of more rapidly growing droplets. The smallest effect, one to five particles, resulted from an exposure of .01 second to a 5-ampere lamp. The sulfur particles are apparently liquid. The sensitivity to light is diminished by the presence of substances which absorb blue or violet rays. The sulfur then appears only at the surface. This effect of light is also inhibited by even the slightest vulcanization of the rubber, and it can therefore serve as an indication of the vulcanization process. The effect is observed as far below the surface as the light penetrates.

During the vulcanization of rubber by phosphorus in ultraviolet light, there appear after prolonged illumination of the optically empty rubber-phosphorus-benzene system, glistening phosphorus particles 0.5 to 2.1 μ in diameter.[28] This formation of nuclei by ultraviolet has its analogy in the transformation of yellow to red phosphorus. A similar turbidity appeared on ultraviolet illumination of a carbon disulfide solution of sulfur containing piperidine pentamethylenedithiocarbamate.

Kirchhof also states [29] that vulcanization of rubber in ultraviolet light by trinitrobenzene or picric acid, especially the former, yields results comparable with those of cold vulcanization. These products, like ordinary vulcanizates, show strong absorption of ultraviolet radiations.

In producing lustrous spread rubberized material, Ditmar [30] spreads the material in the usual way with a benzene solution of a mixture containing crêpe rubber 100 parts, colloidal sulfur 3.5 parts, tetramethylthiuramdisulfide 2 parts, Sulzin (*i.e.*, zinc sulfate-5 NH_3), 7 parts, anhydrous sodium thiosulfate 2 parts, selenium red 1.8 parts and titanium oxide 2 parts. It is then led directly under a battery of quartz mercury lamps, the exposure being for five minutes at a distance of 8 cm. Complete vulcanization results with the production of a non-tacky rubber surface of high lustre.

It was necessary to carry out the process of Bernstein [31] in an inert gas or *in vacuo* to prevent oxidation by the ozone. But when tetramethylthiuramdisulfide is used as an accelerator to minimize the curing time and exposure, and with selenium red as a protective agent, it is possible to cure the spread material in air. Ditmar [32] also showed that ultraviolet radiation has itself an oxidizing action on accelerated rubber mixtures which predominates over the vulcanization. Therefore, from a practical point of view, satisfactory vulcanization is possible only when a red or yellow protective pigment, such as selenium red, is added. With an activator like zinc oxide present in an accelerated mixture, ultraviolet radiation brings about vulcanization in a short time. The duration of the exposure must be carefully controlled to prevent oxidation, under-curing or over-curing. Ultraviolet radiation has the most favorable effect on rubber mixtures accelerated by tetramethylthiuramdisulfide and containing an activator. Surface vulcanization is complete in four and a half minutes without oxidation even in the absence of a protective red pigment.

Surface vulcanization by light is regarded as a true vulcanization process since it has been proved that sulfur must be present. It is believed that the sulfur is activated by the radiation and then enters into reaction with the rubber.[33] Ditmar and

[28] Kirchhof, F., *Kautschuk*, 184 (1927); *Chem. Abs.*, **21**, 2819 (1927).
[29] Kirchhof, F., *Gummi-Ztg.*, **44**, 252 (1929); *Chem. Abs.*, **24**, 750 (1930).
[30] Ditmar, R., *Gummi-Ztg.*, **43**, 1172 (1929); *Brit. Chem. Abs.*, **B**, 294 (1929); *Chem. Abs.*, **23**, 2602 (1929).
[31] Bernstein, G., German P. 262,708, 1912.
[32] Ditmar, R., *Gummi-Ztg.*, **43**, 1172, 2325 (1929); *Chem. Abs.*, **23**, 2602, 4374 (1929).
[33] Ditmar, R., and Grünfeld, O., *Gummi-Ztg.*, **43**, 2801, 2859 (1929); *Chem. Abs.*, **23**, 5612 (1929).

Grünfeld find that, when about 3 per cent of sulfur is present, the addition of organic accelerators can be completely dispensed with. Indeed, many organic accelerators may have an unfavorable action. In most cases, Vulkan colors give excellent shades of color under these conditions, and in combination with other organic and inorganic colors such as selenium red or methylene blue, all kinds of colors and tones can be obtained. In general, ultraviolet vulcanization can be effected in four to eight minutes at 20-90°C., depending upon the support on which the sample rests, the shortest times being obtained on glass. This influence of the support apparently depends upon its heat conductivity and heat capacity, for the higher the temperature prevailing during the process, the more rapid its rate.

Formulas of blue, green, orange, red and brown rubber mixtures which will cure in seven minutes at a distance of ten cm. from the ultraviolet source are given by Ditmar and Preusze.[34]

In patents of the Goodyear Tyre and Rubber Co.[35] the appearance and dirt-resisting qualities of vulcanized rubber are claimed to be improved by exposure to ultraviolet radiation.

On the assumption that the increase in the electrical conductivity of hard rubber on exposure to light and air is a result of the formation of a surface film containing acid, Fry and Porritt [36] carried on experiments to ascertain the mechanism of its formation. It was found that hydrogen sulfide is evolved, the rate of evolution being the greatest in direct sunlight. This may, however, be the result of thermal rather than light action. This evolution of hydrogen sulfide results from a decomposition of the rubber-sulfur compound and occurs in the absence of free sulfur, resins, oxygen and water vapor. Its rate increases with a rise of temperature.

Ultraviolet vulcanization has been employed in the production of surface designs on rubber.[37] A surface of a rubber sheet to be etched is vulcanized by the action of ultraviolet rays or by sulfur chloride, a design is formed on the surface and an etch-resist may be incorporated with the inked parts. A mixture of nitric acid and potassium dichromate is used for etching and the etched sheet is washed with acetone or alcoholic soda solution. Silex and fat-containing fillings should not be present in the rubber.

Rimpel and Hermann [38] state that when strong reducing agents, such as a light-sensitive silver bromide gelatin, are mixed into the rubber, it is possible to form designs or pictures directly by exposure to the light. They do not agree with the suggestion of Defries and Naunton that a discoloration on irradiation is the result of an over-vulcanization produced by light on the surface. When four mixtures, each containing rubber, lithopone and zinc oxide, and the first also sulfur; the second, accelerator; the third, sulfur and accelerator, and the fourth, no addition, were exposed to sunlight for thirty minutes, the first and fourth mixtures remained unchanged, but the second and third became discolored to an equal extent. This indicates that the discoloration depends only on the accelerator and has no direct relation to the state of vulcanization. The accelerator thus behaves like a reducing agent.

[34] Ditmar, R., and Preusze, K. H., *Caoutchouc & gutta-percha*, **26**, 14,762 (1929); *Gummi-Ztg.*, **43**, 2749 (1929); *Brit. Chem. Abs.*, **B**, 863 (1929); *Chem. Abs.*, **24**, 749 (1930).
[35] British P. 404,120, Nov. 10, 1932, to Goodyear Tyre and Rubber Co.; French P. 749,642, July 27, 1933; *Chem. Abs.*, **28**, 685 (1934).
[36] Fry, J. D., and Porritt, B. D., *India Rubber J.*, **78**, 307, 309 (1929); *Chem. Abs.*, **23**, 5613 (1929).
[37] British P. 241,542, Oct. 14, 1924, to Soc. d'Exploitation des Procedes d'Impression Sardou; *Chem. Abs.*, 20, 3590 (1926).
[38] Rimpel, H., and Hermann, P., *Gummi-Ztg.*, **43**, 2270 (1929); *Chem. Abs.*, **23**, 4370 (1929); German P. 448,972; see also Defries, R., and Naunton, W., *Trans. Inst. Rubber Industry*, **4**, 298 (1928); *Chem. Abs.*, 23, 2068 (1929).

Fluorescence of Accelerators. Various accelerators are readily distinguished by their characteristic fluorescence colors in filtered ultraviolet light. When present alone in pale crêpe, some of them may be detected by this method.[39] Even when some other ingredients, such as sulfur, zinc oxide, magnesia, lead oxide, etc., are present, it is possible, in some cases, to distinguish a characteristic appearance. However, with several ingredients present, the fluorescent effect varies with the different combinations, and only when the composition of the mixture is known can the method be employed for the detection of accelerators. Characteristic colors are also obtained after vulcanization, although they are different from those observed in the same mixtures prior to vulcanization.[40] The approximate quantity may be judged within ±5 per cent if the fluorescent light from filtered ultraviolet is passed through an actinometer containing a triphenylmethane dye. Ditmar[41] has listed the fluorescence colors of a number of accelerators. The change of fluorescent color on prolonged irradiation is also of significance.

Nagle[42] employed this method for the study of the pigments used in the industry. In the examination of eight grades of zinc oxide mixed with glycerol, one appeared light green, one light gray-green, one light green-gray, two orange-buff, one bright apple-green, one pale dull violet and one deep violet. After having been kept ten minutes at a white heat, all were green. The same distinctive shades were visible in rubber mixtures when a small proportion was used in vulcanizing the rubber with sulfur, accelerator and lithopone. Even when the rubber mixtures were made dark gray by the addition of carbon black, the individual samples containing zinc oxide could still be distinguished. In lithopones, the range of colors was not so great, the samples appearing deep violet, pale violet, brown or almost white. An examination of rubber imperfectly mixed with zinc oxide and lithopone revealed the characteristic colors of the two pigments and indicated the possibility of determining the distribution of powders in rubber mixtures. The lithopones which appeared deep violet were the most nearly sunproof. Those which appeared white darkened the most rapidly. In filtered ultraviolet light, however, the latter were resistant, indicating the radiation responsible for the darkening to be of wave-length shorter than that transmitted by the filter used (3300-3900A). Mineral oils and Vaseline were fluorescent and phosphorescent, coal-tar showed a faint, yellow-brown fluorescence and sulfur assumed a bronze color. In the form of bloom, it can be readily distinguished by this method. Addition of 1 per cent of coal tar to a black rubber mixture changed its appearance in filtered ultraviolet light from very dark violet to gray-blue. Various tire sections appeared violet, brown-violet, blue, green, yellow and brown-red, since various other added substances exhibited characteristic fluorescences.[43]

Kirchhof[44] reported similar observations, but differed from Nagle in believing the purest grade of zinc oxide to be sulfur-yellow. Since zinc sulfide gives a bright orange color, the fluorescence of lithopone varies with its zinc sulfide content. Among aliphatic substances, vegetable and animal oils, fats and waxes and paraffin hydrocarbons show characteristic colors. Phenols and aromatic acids exhibit particularly bright colors, the intensity apparently increasing with the complexity of the ring. Nitro- groups weaken the fluorescence. Dyes, accelerators and antioxidants are also distinguished by characteristic colors in this manner. The differences in the appearance of various rubbers in filtered ultraviolet depend chiefly upon material which can be extracted by acetone. It was suggested that the method might be of value in following the natural or artificial aging of rubber mixtures by oxidation.

Ditmar[45] employed the method particularly for the study of accelerators. The color of mercaptobenzothiazole, for example, varied with the manufacturer. Kojima and Nagai[46] reported observations on 41 such substances. Morris[47] considered especially the substances important in American manufacture. The personal element plays a large part in the recording of the colors, so that it is necessary to have standard samples available for comparison. Morris believed the color variation in samples of zinc oxide

[39] Ditmar, R., and Dietsch, W., *Chem. Ztg.*, **52**, 388 (1928); *Gummi-Ztg.*, **42**, 1415 (1928).

[40] M. L. P., *Rev. gén. caoutchouc*, **6**, No. 53, 9 (1929); *Chem. Abs.*, **23**, 5612 (1929).

[41] Ditmar, R., *Chem. Ztg.*, **52**, 730 (1928); see also Garner, T. L., [*India Rubber J.*, **77**, 31 (1929); *Chem. Abs.*, **23**, 1772 (1929)] for the identification of antioxidants by this method.

[42] Nagle, P. G., *Trans. Inst. Rubber Industry*, **3**, 304 (1927); *Chem. Abs.*, **22**, 1251 (1928).

[43] Nagle, P. G., *Rubber Chem. & Tech.*, **1**, 284 (1928).

[44] Kirchhof, F., *Kautschuk*, **4**, 24 (1928); *India Rubber J.*, **75**, 791 (1928); *Chem. Abs.*, **22**, 2291 (1928).

[45] Ditmar, R., *Caoutchouc & gutta-percha*, **28**, 15,685 (1931); *Chem. Abs.*, **25**, 6017 (1931).

[46] Kojima, K., and Nagai, I., *J. Rubber Soc. Japan*, **2**, 260 (1930); *Chem. Abs.*, **25**, 3871 (1931).

[47] Morris, V. N., *Ind. Eng. Chem.*, **26**, 107 (1934).

to be related to a certain extent to the particle size. Well-vulcanized rubber shows a yellow fluorescent color of fairly strong intensity, but decidedly undercured rubber fluoresces only slightly. Rubber loses its fluorescence almost completely after an hour in direct sunlight. For this change, oxygen is not essential. In general, no definite relation is apparent between the optimum physical properties of rubber and the intensity of its fluorescence.[48]

Fluorescence tests may also be employed in judging the progress and uniformity of vulcanization. The light emitted by mixtures containing three to eight per cent of sulfur increases with the state of vulcanization. The fluorescence changes are accelerated by zinc oxide.[49] With ten per cent or more of sulfur, when semi-ebonites are formed, the fluorescence becomes brown-red and less intense. Undercured rubber mixtures, in general, show relatively weak fluorescence and overcured ones a strong fluorescence, greenish for rubber and sulfur mixtures and yellowish-green for accelerated mixtures. Excessive overcuring may make the fluorescence yellow. The fluorescence of Neoprene also increases during vulcanization without sulfur but less markedly than in the case of rubber. Oberto[50] has also described the changes in fluorescence of vulcanized rubber during aging, natural or artificial. In the initial stages (one minute in sunlight), it changes to violet, even before an alteration of mechanical properties can be noted. Later it becomes more intense, finally changing to ochre or red, depending upon the sulfur content, at complete deterioration (ten hours of exposure). The presence of other substances may complicate the fluorescence effects.

Light and the Oxidation of Rubber

In reviewing this topic, Shepard, Krall and Morris[51] state that as early as 1865, Spiller[52] proved that oxygen functions in the change undergone by strained rubber in light. Burghardt[53] believed that light alone would injure perfectly good normal vulcanized rubber only when acting in conjunction with other destructive agents. Fickendey[54] showed that samples exposed to direct sunlight in sealed tubes in hydrogen, nitrogen and carbon dioxide remained unchanged for weeks, although rubber exposed under oxygen became sticky. Ahrens,[55] Peachy and Leon,[56] and Henri[57] considered sun-checking or sun-cracking an oxidation process aided by both light and heat.

Asano[58] observed that when rubber is exposed to ultraviolet light under carbon dioxide, nitrogen or hydrogen, it is converted into two products of much the same composition. One was a white, opaque, brittle, polymerized substance, insoluble in benzene. The other was a depolymerized, tacky product of reduced viscosity. Similar behavior was observed during exposures in air. Asano believed that radiations longer than 3100A had no significant effect, and that these physical and chemical changes were most rapid and profound under the influence of wave-lengths between 2250 and 2000A. Some dyes, however, sensitize rubber to longer wave-lengths. These changes were largely independent of oxidation, which occurred to a considerable extent only in sunlight, and caused tackiness, followed by brittleness. The ultimate products were insoluble in boiling benzene, chloroform, alcohol or acetone, and contained 14.6 per cent of oxygen. The action

[48] For a general review of fluorescence tests for rubber, see Hauser, E. A., and Le Beau, S., *Kautschuk*, **10**, 113 (1934); Krahl, M., *Kautschuk*, 159, 180 (1927).

[49] Oberto, *Gomma*, **1**, 157 (1937); *Chem. Abs.*, **32**, 3198 (1938).

[50] Oberto, S., *Rubber Tech. Conf. London, Preprint No. 75*, May, 1938; *Chem. Abs.*, **32**, 8212 (1938).

[51] Shepard, N. A., Krall, S., and Morris, H. L., *Ind. Eng. Chem.*, **18**, 615 (1926).

[52] Spiller, J., *J. Chem. Soc.*, **18**, 44 (1865).

[53] Burghardt, C. A., *J. Soc. Chem. Ind.*, **2**, 119 (1883).

[54] Fickendey, E., *Kolloid Z.*, **9**, 81 (1911).

[55] Ahrens, F., *Kunststoffe*, **3**, 478.

[56] Peachy, S. J., and Leon, M., *J. Soc. Chem. Ind.*, **37**, 56T (1918).

[57] Henri, V., *Caoutchouc & Gutta-percha*, **7**, 4372 (1910).

[58] Asano, K., *India-Rubber J.*, **70**, 307, 347, 389, 395 (1925); *Chem. Abs.*, **19**, 3616 (1925).

involved an initial depolymerization, with subsequent accelerated oxidation of the depolymerized product. The oxidation was induced by wave-lengths shorter than 5000A, and the depolymerization by longer wave-lengths. Elimination of the infra-red rays by a water filter did not alter the action of sunlight. The intensity of light governed the rapidity of the changes. Asano also alluded to the deleterious action of ozone.

Williams [59] definitely showed that 5 grams of emery-wheel buffings of a pure gum inner tube absorb oxygen more rapidly in sunlight (0.93 cc. per hour) than in darkness (0.13 cc. per hour). Light had, however, little effect upon unstrained strips of the same rubber. The success in the case of the buffings was due to the fact that the fresh surfaces clung together in such a manner as to keep the small particles in a strained condition.

It was claimed by de Jong [60] that in a quartz vessel exposed to sunlight in the Dutch East Indies, a benzene solution of crepe rubber absorbed a considerable volume of air. In later experiments with less intense sunlight in Holland, the same process occurred behind glass, but less rapidly. In eight days, 25 cc. of air were completely absorbed by 325 cc. of solution. de Jong claimed also that after six days of exposure in sealed tubes under nitrogen, a 1.05-per cent solution of rubber in benzene absorbed 2.5 per cent of nitrogen and that the absorption of this gas by the hydrocarbon from balata gutta-percha after purification with petroleum ether also occurs. However, nitrogen absorption by rubber has been denied by Howard and Hilbert.[61] Dogadkin and Panchenkov [62] observed that on irradiation of rubber solutions in nitrogen, the interfacial tension against water did not change. When irradiated in air, it was lowered and reached a constant value in two hours.

Bondy and Lauer [63] found, in agreement with Staudinger and Leupold, that rubber solutions do not autoxidize in darkness. In light, the solutions decomposed in the same manner whether or not the natural antioxidant was present. There was no decomposition when the exposures were made in nitrogen; only in light and air were positive results attained.

Williams [59] also showed that the exposure of strips of a vulcanized gray side-wall stock stretched to an elongation of 5 per cent, and exposed in air or oxygen (but not in evacuated tubes) to July sunlight daily for two weeks appeared slightly wrinkled. Upon releasing the strain, the wrinkled appearance became pronounced, showing that a non-elastic skin had formed on the surface. The weight had increased slightly. The skin had a glazed appearance, was almost inelastic but not brittle and was soluble in alcohol. The surface beneath appeared unchanged and no decrease in tensile strength could be observed. Light-colored rubber will form, in some cases, a pronounced skin in two days of exposure to the sun.

Tests by Williams with various colored filters indicated that the short wave-lengths of visible light from a tungsten lamp were most effective in producing surface oxidation. White light produced the heaviest skin. The amount of oxidation was directly dependent upon the intensity of the light. A mercury lamp placed ten inches from the strip elongated at about 10 per cent produced a pronounced surface oxidation in three hours. If, however, the mercury lamp is placed two to three feet from the strip no skin formed. Instead, after one or two hours, small cracks began to appear in the surface of the rubber. These continued to

[59] Williams, I., *Ind. Eng. Chem.*, **18**, 367 (1926).
[60] de Jong, A. W. K., *Rec. trav. chim.*, **51**, 133 (1932).
[61] Howard, L. B., and Hilbert, G. E., *J. Am. Chem. Soc.*, **59**, 214 (1937).
[62] Dogadkin, B., and Panchenkov, G., *Kolloid-Z.*, **65**, 350 (1933); *Chem. Abs.*, **28**, 1890 (1934).
[63] Bondy, H. F., and Lauer, G. G., *Ber.*, **66B**, 1611 (1933).

increase in size and number, but the surface between the cracks remained unchanged except on prolonged exposure. This type of oxidation, due it was believed to ozone, is characterized by extreme rapidity and by a negligible increase in weight.[64] In direct ozonizing tests, it was necessary to reduce the concentration of ozone to about one part in 50,000 of air in order to reduce the speed of cracking to a point at which observations could be accurately made. Surface oxidation appears to be to some extent an efficient protection against even a relatively high concentration of ozone, since this cracking was not observed in samples which had been exposed ten inches from the lamp. Checking can be retarded by catalyzing the surface oxidation by means of copper salts.[65] Compounds containing zinc oxide are more easily protected than pure gum type compounds.

The basic components of the acetone-soluble material from rubber account for the antioxidant effect of both rubber and balata, according to Bondy and Lauer.[66] The acids, amino-acids and bases of the serum and phenols have a slight antioxidant effect. The neutral components and acid amides are inactive in this respect. Heating rubber or balata resin at 120°C. increases its protective action against ultraviolet light. Those rubber solutions which had the deepest brown color had the least tendency to autoxidize. Further experiments showed that a dye present in the rubber retards autoxidation by absorbing the active radiations. Tests of known dyes proved that some have a marked protective action by internal filtering, but others were only slightly protective.

Bondy,[67] irradiated purified balata in the solid state in air with sunlight and with ultraviolet light, determining the extent of autoxidation by measuring the viscosity of Tetralin solutions of a concentration corresponding to 0.2 molecule of isoprene, before and after irradiation, *i.e.*, by the general method of Staudinger. Rubrene and dehydrorubrene had almost no effect on the reaction. Bidiphenylene-ethylene and β-naphthoquinone were active antioxidants, but anthraquinone showed strong proöxygenic influence. Paraquinone had no effect and acenaphthenequinone almost none. Aldol-α-naphthylamine as well as an acetone extract of rubber had weak, and phenanthrenequinone or α-naphthoquinone strong polymerizing influence. The most highly colored compounds were the strongest antioxidants. Aldol-α-naphthylamine reduced slightly the polymerizing action of α-naphthoquinone.

When balata in solution was irradiated, rubrene and dehydrorubrene were distinct proöxygens, whereas bidiphenylene-ethylene and an acetone extract of rubber were without influence. Passage of the light through a toluene filter had no influence on its oxidizing action on balata or acetone-extracted rubber exposed to the air. All substances which acted as antioxidants when added to the rubber showed the same property when employed as external filters. Azobenzene and α-benzeneazo-β-naphthylamine also prevented autoxidation and α-naphthoquinone, phenanthrenequinone and alizarine retarded it greatly when their solutions were used as filters. A colored substance which absorbs active radiations inhibits autoxidation only if it is soluble in balata or acetone-extracted rubber. The antioxygenic power of an acetone extract of rubber depends in part upon its brown color, for even in very low concentrations, *e.g.*, 0.1 per cent in toluene as a light filter, it still retarded autoxidation. This does not mean, however, that the antioxygenic power depends only on the colored components. By means of filters, the spectral region

[64] See also van Rossem, A., and Talen, H. W., *Kautschuk*, **7**, 79, 115 (1931); *Chem. Abs.*, **25**, 5795 (1931).
[65] This could not be confirmed by van Rossem, A., and Talen, H. W., *Kautschuk*, **7**, 79, 115 (1931); *Chem. Abs.*, **25**, 5795-6 (1931).
[66] Bondy, H. F., and Lauer, G. G., *Ber.*, **66B**, 1611 (1933).
[67] Bondy, H. F., *Rev. gen. caoutchouc*, **11**, No. 1, 6, 9 (1934); *Chem. Abs.*, **29**, 4207 (1935).

which is active in autoxidation in sunlight was found to lie between 3000 and 4800A. In this ultraviolet region, the activity was apparently uniformly distributed. Sunlight and ultraviolet light were found to be similar in effects, in spite of the fact that ozone is formed only by the shorter wave-length ultraviolet light absent from sunlight.

The rate of oxidation of vulcanized rubber in ultraviolet light and air or oxygen increases with the time of vulcanization. It is greatly increased by extraction with acetone. It varies greatly with the kind of rubber, vulcanized crepe oxidizing far more rapidly than vulcanized Para rubber, probably because ultraviolet light penetrates the former much more readily than the latter.[68] The difference in the rate of oxidation of unextracted and extracted vulcanized rubber is probably closely related to the condition of the sulfur and to the absorption of ultraviolet light, for it is known that ultraviolet light is completely absorbed by a vulcanized mixture which reflected it before vulcanization and that carbon disulfide containing sulfur absorbs ultraviolet light while carbon disulfide alone transmits it. This suggests a means of determining whether sulfur is chemically combined or in solution and suggests that chemical combination occurs during vulcanization. The primary yellow products of oxidation in ultraviolet light are converted by boiling dilute sulfuric acid to the same brown substances which are obtained on oxidation in darkness at 70°C. The immediate onset of oxidation in ultraviolet light is in contrast to the induction period in oxygen alone. The gain in weight occurring during the oxidation in ultraviolet light ceases long before the oxygen reaches the proportion represented by C_5H_8O. The rate of oxidation of vulcanized rubber in ultraviolet light and air at 40° to 45°C. is about three times that in air at 70°C. in darkness.

Kirchhof [69] later used the ability of the natural water extract of raw rubber to reduce an ammoniacal silver nitrate solution at room temperature in detecting the effect of light on rubber. After a brief exposure to light, crêpe still reduces the reagent with dispersion of silver throughout the rubber, whereas water-extracted crêpe or crêpe bleached with sodium bisulfite does not reduce the reagent. After prolonged exposure crêpe no longer reduces the reagent, because light in conjunction with oxygen destroys the reducing substances (probably sugars). There is also a bleaching effect, perhaps because of the formation of hydrogen peroxide. Ultraviolet light has the same effect as sunlight, except that there is a yellowing instead of a bleaching, perhaps because of peroxide formation.

In sunlight and ultraviolet light, purified gutta-percha slowly turns yellow and on treatment with ammonia-silver nitrate turns brown because of peroxide formation. Samples of pale crêpe with no reducing action were immersed in solutions of hydroquinone, phenyl-α-naphthylamine and the commercial antioxidants, Parazone ND and MB, dried in darkness, and exposed to ultraviolet light. There was no visible change except with the phenylnaphthylamine in which case yellowing occurred. On treatment with ammonia-silver nitrate, there was reduction with hydroquinone and Parazone, while with the phenyl-α-naphthylamine and Parazone MB, there was no reduction, even by the unexposed part. Since hydroquinone and Parazone have a marked protective action on rubber exposed to light, this action is related directly to the reducing power. The stability of hydroquinone and Parazone toward light accounts for the continued protective effect at low concentrations.

[68] Kirchhof, F., *Kautschuk,* 239, 256 (**1927**); *Chem. Abs.,* **21,** 3766 (1927).
[69] Kirchhof, F., *Kautschuk,* **9,** 70 (1933); *Chem. Abs.,* **27,** 4126 (1933).

Dogadkin and Balandina [70] irradiated rubber with ultraviolet light under water in quartz flasks. Aqueous extracts were then prepared and tested for oxidation products which at 100°C. reduce gold salts to rose-colored colloidal gold. Unexposed pale crêpe and smoked sheet gave no reduction, but after ultraviolet irradiation they each reduced gold chloride. In each case on continued irradiation the concentration of colloidal gold increased to a maximum and then diminished. The electrical conductivity of the extracts, after diminishing slightly to a minimum after a certain period of irradiation, increased continuously.

Defries and Naunton [71] investigated the effect of sunlight on the color of cured and uncured accelerated mixes. Rubber mixtures containing crêpe 100, zinc oxide 10, barium sulfate 100, and sulfur and accelerator (diphenylguanidine, di-*o*-tolylguanidine, triphenylguanidine, mercaptobenzothiazole, thiocarbanilide, aldehyde-ammonia, tetramethylthiuramdisulfide and zinc diethyldithiocarbamate) were exposed to ultraviolet light. With all accelerators, exposure before curing gave no visible effect, but, when cured, the previously exposed samples were much darker than ones not so treated before curing. These darker samples could not be lightened by irradiation. Ultraviolet light induces oxidation of the vulcanizates. When the samples were undercured, a second exposure to light intensified the darkening. The results indicate, first, that exposure of uncured samples causes a surface vulcanization, second, the discoloration is an effect of a surface overcure produced by normal vulcanization superimposed on an already slightly vulcanized surface and third, bleaching of vulcanizates by light results from oxidation, since it can be minimized by exposure in an inert gas and can be produced by oxidizing agents. When, however, there is an excess of vulcanizing agent to permit after-vulcanization, a subsequent exposure induces further darkening instead of bleaching.

Accelerated Weathering Tests

Artificial aging of vulcanized rubber was thought by Pelizzola [72] to be identical with natural aging, from both chemical and physico-mechanical points of view. Asano [73] directed experiments toward an understanding of the fundamental processes involved. As an aging test, he recommended that samples be maintained at 71°C. in a steady current of air and at the same time be exposed to ultraviolet light until the changes are of sufficient magnitude to compare the stress-strain curves and the chemical composition. By this test, rubber-insulated wire cracked after an hour, although it remained unchanged after fifteen hours in darkness.[74]

It must be noted that light is but one of several aging factors employed in accelerated aging tests, although it is the only one requiring mention here. Jecusco [75] placed a Uviarc in the accelerating cabinet 7 cm. above the reel which held the samples of rubber so that its rays fell at right angles to the narrow part of dumbbell samples held by clips. The oven was of a standard construction 3 feet deep, 5 feet high and 4 feet wide, with walls filled with 2-inch asbestos and air insulation. It had a specially constructed wooden reel, 24 inches in diameter

[70] Dogadkin, B., and Balandina, V., *Kautchuk,* **9,** 146 (1933); *Rubber Chem. Tech.,* **7,** 18 (1934); *Chem. Abs.,* **28,** 4936 (1934).
[71] Defries, R., and Naunton, W. J. S., *Trans. Inst. Rubber Ind.,* **4,** 298 (1928); *Chem. Abs.,* **23,** 2068 (1929).
[72] Pelizzola, C., *Giorn. chim. ind. applicata,* **4,** 458 (1922); *Chem. Abs.,* **17,** 1559 (1923).
[73] Asano, K., *India-Rubber J.,* **70,** 307, 347, 389 (1925); *Chem. Abs.,* **19,** 3616 (1925).
[74] Asano, K., *Mem. Kyoto Univ.,* No. 3, 267, 1926; *Gummi-Ztg.,* **41,** 1576; *Chem. Abs.,* **21,** 2398 (1927). For other early tests, see also Jacobs, S., *Caoutchouc & gutta-percha,* **25,** 14,110 (1928) and Krahl, M., *Kautschuk,* 159, 180 (**1927**); *Chem. Abs.,* **21,** 2816 (1927).
[75] Jecusco, F. P., *Ind. Eng. Chem.,* **18,** 420 (1926). Recent aging apparatus is described by Walter, P., *Rev. gén. caoutchouc,* **14,** No. 134, 26 (1937).

and 28 inches long, having eight arms and eleven wooden cross rods one inch in diameter forming an open reel of the squirrel-cage type. This revolved on a shaft at 26 r.p.m. Underneath a perforated floor plate were enough electric heating units to give a temperature of 50 to 100°C., automatically controlled by a thermostat. Underneath the floor plates on either side of the oven were large adjustable air shutters and baffle plates to admit the circulation of air through the heaters. There was also a top vent with damper control.

When both light and heat were used, a sample gave twice as much acetone-extract as after the heat test alone. In the heat test there was merely a pronounced darkening at the end of 144 hours, but with light and heat, the sample began to fog after three hours, a brownish tint began to appear at six hours, and after nine hours it was decidedly brown. After 21 hours the sample started to darken not unlike a sample heated alone for 144 hours. It gradually became darker up to 39 hours when it threw a purplish hue over the brown. This colored coating was insoluble in all common organic solvents and in caustic soda solution. Even after three hours, the surface was somewhat checked. This was pronounced at 39 hours. It began to crack at six hours. A decided stiffening became apparent at 18 hours and continued to the end of the test. The loss of weight was, however, decreased in this test.

Other rays than those shorter than the 2250A (found active by Asano, who used only raw rubber) were effective in the aging of vulcanized rubber. Even sunlight was effective. Sunlight appeared to act in spurts. At 90°F. the first spurt from the cold Uviarc starts at the beginning of irradiation and continues until the breaking stress has been reduced from the initial 2260 to 1575 lbs. per square inch (fifteen hours) after which the deterioration is slow. At higher temperatures the spurts are more frequent and the delays shorter. The cause of these delays in the aging may be the formation of a protective coating. From filter experiments, it was concluded that green rays which have apparently no action on fresh rubber, have a tremendous effect on oven-aged rubber. Infrared rays showed an effect on both fresh and "activated" rubber. Apparently all rays have an action at some stage on the degradation of vulcanized rubber. The results seemed to indicate that light did not give a quantitative measure of the ability of rubber to withstand weathering.

Others, however, believed ultraviolet light to give a fair indication [76] of the ability of samples of raw or vulcanized rubber to withstand exposure to sunlight under natural conditions. The visible changes of individual samples are only relative and an adequate judgment of their aging properties requires the simultaneous exposure of samples of known aging properties. The ultraviolet light test is also useful in predicting the behavior of dyes in rubber.

Krahl [77] found ozonized air to have little effect on sharply bent rubber mixtures unless they were simultaneously exposed to ultraviolet light. Then they soon cracked at the bent sections. The resistance to such attack varies with different mixtures. In general, dark-colored mixtures crack sooner than light-colored ones, and overcured mixtures crack sooner than normally cured ones. In the aging test, Krahl exposed the samples intermittently to ultraviolet light so that their temperature did not rise to a point at which thermal changes become significant. He accomplished this by using a water-cooled rotating drum on which the radiation falls over one longitudinal section. The friction strength of insulating tapes in

[76] K. L., *Gummi-Ztg.*, **41**, 417 (1926); *Chem. Abs.*, **21**, 510 (1927).
[77] Krahl, M., *Kautschuk*, 159, 180 (1927); *Chem. Abs.*, **21**, 2816 (1927).

this test [78] first increased with the time of exposure and then decreased progressively until it was but negligible. In comparative tests in which the samples were merely heated in air at 70°C., the strength decreased progressively from the beginning.

More complicated tests have been devised. In one,[79] during each revolution of a wheel about eight feet in diameter, the samples were successively submitted to immersion in water, desiccation by a hot or cold air blast, ultraviolet radiations, ozone, etc.

Yamazaki [80] exposed samples of vulcanized rubber to sunlight filtered through one of four glass plates transparent to 2900, 3130, 3300 and 4360A, respectively. The effect of the unavoidable heating was studied in control experiments by air-heating at 70-71°F. in darkness for 150 hours. The color of vulcanized rubber became darker by air-heating, but when exposed to sunlight at 60-70°F. the change in color was far more remarkable. The higher the degree of vulcanization, the greater the change in color. Moreover, the rubber was hardened by the action of light. The shorter the wave-lengths and the higher the temperature, the sooner did hardening occur. The action of the rays of wave-length greater than 4300A was very weak except in the case of overvulcanized rubber which was noticeably hardened. The acetone extract increased with the time of exposure, the rate of increase being less the longer the wave-lengths used. In some cases, the acetone extract reached a maximum and then decreased. It was considered that the increase in acetone extract was due principally to the oxidation of the rubber. The subsequent decrease, when observed, was attributed to the conversion of a part of the oxidized product into substances insoluble in acetone. The action of light and heat also caused a remarkable decrease in the free sulfur. The time of vulcanization of rubber-sulfur mixtures had a marked effect on the aging properties.

The deterioration due to sunlight was great even in winter and was very marked in the spring at 60°F. The outer layers of test-pieces exposed to sunlight were quite brittle and inelastic but the inner layers were still fairly good. Test-pieces subjected to Geer oven tests showed but little difference between the outer and inner layers.

Differences between the effects of sunlight and a quartz mercury arc were noted by Weightman [81] in the case of vulcanized mixtures, particularly those which contained reclaimed rubber. Some samples of the latter which failed in service were comparatively resistant to ultraviolet rays. A violet carbon arc gave results more similar to those of sunlight. Temperature, humidity and air supply should be controlled during the test.

McKee and Depew [82] found that overcured mixtures become surface checked sooner than the corresponding undercured mixtures in the light test, although the reverse was the case in darkness. Paraffin and zinc oxide retarded this action of light.

The varied conditions under which rubber is used make it particularly difficult to find any one suitable artificial aging test. Bierer and Davis [83] believed that

[78] Krahl, M., *Gummi-Ztg.*, **42**, 965 (1928); *Chem. Abs.*, **22**, 1495 (1928).
[79] French office nationale des recherches et inventiones, *Rev. gen., caoutchouc*, No. 29, 11 (1927); *Chem. Abs.*, **21**, 1899 (1927).
[80] Yamazaki, T., *J. Soc. Chem. Ind. Japan*, **30**, 804 (1927); *Brit. Chem. Abs.*, **B**, 615 (1928); *J. Soc. Chem. Ind. Japan*, **31**, 233, 243 (1928); *Chem. Abs.*, **22**, 3066 (1928); Yamazaki, T., and Okuyama, K., *J. Soc. Chem. Ind. Japan*, **32**, 367B (1929); *Brit. Chem. Abs.*, **B**, 250 (1930); *Caoutchouc & gutta-percha*, **27**, 15,016 (1930).
[81] Weightman, H. E., *Rubber Age (N. Y.)*, **23**, 75 (1928); *Chem. Abs.*, **22**, 2290 (1928).
[82] McKee, R. H., and Depew, H. A., *Ind. Eng. Chem.*, **20**, 484 (1928).
[83] Bierer, J. M., and Davis, C. C., *Ind. Eng. Chem.*, **21**, 1008 (1929). See also Karpinsky, Z., *Przemysl Chem.*, **21**, 202 (1937); *Chem. Abs.*, **31**, 8989 (1937).

neither the Fade-Ometer (see Chapter 32) nor the ultraviolet light tests truly duplicate the effects of sunlight.

In the aging of rubberized balloon fabrics, according to Barr,[84] there are essential differences between the effects of ultraviolet light and of tropical sunlight. Losses in tensile strength of the fabrics were similar, but though the permeability of the samples exposed to ultraviolet light remained unaltered, those exposed to sunlight became extremely permeable and their sulfuric acid contents became relatively large. Ultraviolet light caused a disproportionately great deterioration of the cotton, whereas tropical sunlight acted relatively rapidly on the rubber and sulfur with the formation of sulfuric acid which in turn attacked the cotton. Organic dyes and inorganic pigments protect the cotton from sunlight, lead chromate giving the best results.

Graffe[85] finds that in the light test the increase in acetone extract and the gain in weight are parallel up to an advanced stage of deterioration, so that the progress of the aging can be followed by the gain in weight. By the use of intermittent exposures, it was found that at certain stages of the aging process ultraviolet light accelerates a subsequent autoxidation in the air.

Tanaka, Kambara and Fujita[86] state that the original cold elongation of vulcanized rubber is increased by exposure to ultraviolet rays.[87]

Ebonite that had been exposed under glass for fifteen years to light showed superficial cracking and masses of a whitish deposit.[88] The majority of samples showed a content of combined sulfur greater than that corresponding to the formula C_5H_8S. The exposure appeared to have caused oxidation of part of the caoutchouc to "resins," leaving a residue richer in sulfur. Certain of the samples containing organic softening ingredients such as palm pitch or carnauba wax had deteriorated less than the others.

Exposure of semi-ebonite to ultraviolet radiations[89] caused small increases in weight with the formation of a very thin hard and lustrous skin. Exposure outdoors also increased the weight and brought about surface changes. The effects of antioxidant both on exposure to ultraviolet rays and outdoors were relatively small.

Following an induction period, the electrical resistivity of the surface of low-grade loaded hard rubber and ebonite on exposure to light, air and humidity drops rapidly. It reaches a saturation point at about 10^7 to 10^8 ohms, after which it continues relatively slowly.[90] Ebonite, though initially superior to low-grade loaded hard rubber, deteriorated more rapidly and to a greater degree. After removal from the light, the resistivity of the low-grade loaded hard rubber increased slowly. The surface resistivity of ebonite was sensitive to the relative humidity during measurements, except during the induction and saturation stages. When the relative humidity during exposure was varied, there was found a maximum rate of deterioration of ebonite at 70-90 per cent relative humidity, indicating that both

[84] Barr, G., *Trans. Inst. Rubber Ind.*, **5**, 31 (1929); *Chem. Abs.*, **23**, 5350 (1929). Tests for rubber composition soles are described by Dock, E. H., *Trans. Inst. Rubber Ind.*, **13**, 160 (1937).

[85] Graffe, L., *Caoutchouc & gutta-percha*, **28**, 15,714, 15,797 (1931); *Chem. Abs.*, **26**, 622, 1152 (1932)

[86] Tanaka, Y., Kambara, S., and Fujita, H., *J. Soc. Chem. Ind. Japan*, **37**, 522 (1934); *Brit. Chem. Abs.*, **B**, 1071 (1934).

[87] For further general reviews of aging tests, see Garner, T. L., *Ind. Chemist*, **7**, 295 (1931); Moureu, C., Dufraisse, C., and Lotte, P., *Ind. Eng. Chem.*, **22**, 549 (1930); Jackson, H., *Trans. Inst. Rubber Ind.*, **10**, 292 (1934); *Chem. Abs.*, **29**, 3871 (1935); Carpenter, A. W., *India Rubber World*, **95**, No. 6, 39, 44, 48 (1937); Saito, S., *J. Soc. Rubber Ind. Japan*, **6**, 525 (1933).

[88] Scott, J. R., *Res. Assoc. British Rubber Mfrs.*, **5**, 2 (1936); *Brit. Chem. Abs.*, **B**, 338 (1936).

[89] Gibbon, P. A., *Trans. Inst. Rubber Ind.*, **10**, 494 (1935); *Chem. Abs.*, **29**, 6468 (1935).

[90] Church, H. F., and Daynes, H. A., *J. Rubber Research*, **6**, 13 (1937); *Chem. Abs.*, **31**, 5211 (1937).

dry and saturated atmospheres had a retarding effect. In artificial light (15 cm. from a 100-watt gas lamp), deterioration was slower than in bright north light, but, in the case of ebonite, the results were the same when expressed in standard hours measured by a photographic exposure meter. The low-grade hard rubber deteriorated relatively less rapidly in artificial light, probably because of a recovery of its resistivity value. Accelerated and artificial light aging tests cannot yet be accepted as criteria of true relative stabilities in sunlight.

Turner[91] studied the influence on the sun-cracking of vulcanizates exerted by quantities of coloring matter too small to alter significantly the characteristics of the white base mixture. Inorganic and organic colors (both soluble and insoluble in rubber) including blue or black, red, green and yellow ones, were tested in two types of non-blooming white vulcanizate exposed under low stress (6 or 7 per cent elongation) to sunlight. In all cases, surface cracking took place much sooner when a coloring agent was present. Next to white vulcanizates, the blue ones were the slowest to crack. The resistance of the white vulcanizates was attributed to their ability to form a protective skin more readily than do the colored products. The coloring materials were thought to absorb wave-lengths which might otherwise be absorbed by the rubber and lead to the formation of the skin. A translucent vulcanizate absorbs more light than does a white one and therefore forms a protective skin more readily than does a corresponding opaque one. This was shown by the fact that a vulcanizate containing titanium dioxide cracked sooner than a corresponding one containing an equal volume of barium sulfate and having a more pronounced film. This may explain the beneficial effect of magnesium carbonate.

Protection of Rubber

According to Schopper,[92] solutions of coumarin derivatives, *e.g.*, a 1-per cent solution of dimethylamino-methylcoumarin, may be used to absorb ultraviolet rays and protect the fabric of balloons from damage by sunlight. Jakowsky[93] calls attention to the opaqueness of the carbon black used as a reinforcing agent in rubber and notes the general belief that this property affords rubber of greater durability by preventing the penetration of light, especially ultraviolet rays, into rubber.

Shepard, Krall and Morris[94] attempted to determine the influence of various compounding ingredients, including fillers, softeners, accelerators, and an antioxidant, on sun-checking. They stretched the rubber to an elongation of 12.5 per cent and obtained checking of susceptible samples within 24 hours, although unstretched samples were not checked for months when exposed to sunlight. Dumbbell strips, 5 mm. thick, stretched on frames, were hung by ropes from the roof where they could revolve in the wind. It was concluded that, through the proper selection of rubbers, reclaim and compounding ingredients, it is possible to reduce to a marked extent the tendency of rubber products to check and crack. The maximum results from a checking standpoint would be obtained by using only those materials in compounding that are protective in their action. Unfortunately, however, selective pigmentation cannot usually be resorted to without the sacrifice of desirable physical properties. Carbon black, for example,

[91] Turner, H., *Trans. Inst. Rubber Ind.*, **10**, 21 (1934); *Chem. Abs.*, **28**, 7591 (1934).

[92] Schopper, T., *Gummi-Ztg.*, **29**, 1250 (1915); *Z. angew. Chem.*, **28**, *Ref.* 644 (1915); *J. Soc. Chem. Ind.*, 356 (1916).

[93] Jakowsky, J. J., *Bureau of Mines Tech. Paper* 351 (1924); see also Bradshaw, H., *Ind. Eng. Chem.*, **19**, 1110 (1927).

[94] Shepard, N. A., Krall, S., and Morris, H. L., *Ind. Eng. Chem.*, **18**, 615 (1926).

has no protective action, and even in small quantities offsets the protective action of other pigments; but for tread stocks this pigment is highly desirable for toughness, resistance to tear and abrasion. Other characteristics, such as the blooming of certain protective materials, make their commercial application very difficult. There is little difference between the accelerators triphenylguanidine, diphenylguanidine and methylene-*p*-toluidine. Benzidine (the only antioxidant tested) has to be added to the extent of 3.6 per cent to give complete protection for a week. The solubility of a material in rubber plays a prominent part in its value as a protective agent. Mineral rubber and other asphaltic substances have no beneficial effect. Rosin and pine pitch are detrimental. Vegetable oils have little effect. Paraffin has a stronger protective action than Vaseline, but more than 2 per cent is necessary for complete protection. A light engine-oil is inferior to Vaseline. Crude Montan wax is but little if any better than asphaltic softeners. When refined, it is intermediate between Vaseline and paraffin. Zinc oxide and lithopone do not protect to the same extent as whiting and clay which are of low covering power. Low-grade off-color rubbers are not more susceptible to sun-checking than are high-grade rubbers. A white stock loses much more in resistance when made gray or black.

Dyestuffs capable of absorbing ultraviolet light were added by Porritt and Dawson [95] who also used polyphenols and aminophenols as antioxidants. Lister found dragon's blood resin to offer no protection against oxidation in cured rubber proofing exposed to the weather and to ultraviolet light.[96]

Preservative paints or coatings for application to rubber goods may be made with a medium capable of swelling the rubber and a material, such as mineral rubber, to increase the viscosity and afford some mechanical protection. Small quantities of antioxidants, such as aldol-α-naphthylamine, and of yellow or red substances such as Oil Red S may be added.[97]

Henri [98] stated that litharge and antimony sulfide accelerate the changes produced by ultraviolet rays. Copper salts, even in traces, are bad,[99] while powdered glass, according to Ditmar,[100] protects in direct proportion to the amount present. Zinc oxide accelerates oxidation but not in any direct relation to its percentage.

Kreusler and Budde [101] dipped vulcanized rubber articles into a paraffin bath at 100°C. to render them resistant to light and air. Himmelbauer and Co.[102] used Vaseline or ceresin wax. Ahrens [103] stated that in 1899 he added ceresin to a tread stock on the mixing mill and then exposed tires with half and half tread, one-half containing ceresin and the other not. The protective action observed in the presence of ceresin was ascribed to the chemically inert bloom or coating of ceresin. Chertoff [104] uses certain vegetable oils, including palm, rosin, pine and turpentine oils, with resins (dammar, rosin, copal), to prevent rapid deterioration and hardening of rubber with age. Paraffin, mineral and other non-drying oils have also been suggested by Repony.[105]

Mazurek and Josse [106] recommended that fabric for the Gordon Bennett Cup balloons be colored red or yellow to protect the mixture from light, and also that it be impregnated on both sides with Revertex mixture. Coe [107] combines chlorophyll green with rubber in such manner as to exclude all wave-lengths of light except those transmitted between 5270 and 6500A.[108]

Bonding Rubber to Other Materials. Livings and Lacey [109] described a method of bonding unvulcanized rubber to metal, glass, or ebonite, by preparing a bonding surface on the rubber by exposure to ultraviolet rays. Rubber so treated may also be used to bond together materials of dissimilar or similar nature, such as metal and wood or metal and metal. The rubber is finally subjected to pressure and vulcanization.

In joining vulcanized rubber compositions to metals, glass, molded phenol condensation products, hard rubber, etc., Morse [110] inserts a sheet of rubber composition containing a vulcanizing agent such as sulfur, zinc oxide and glue. To reduce tackiness one surface of it is previously exposed to light from a carbon arc for a period sufficiently beyond that at which the tackiness of the rubber may be increased. It is inserted between the materials to be joined, with the unexposed surface of the sheet adjacent to the first-mentioned rubber composition and the sheet of rubber composition is vulcanized in place.

Chlorinated Rubber. In a patent for the production of plastic products from india-rubber, Dyche-Teague [111] states that rubber which has been thoroughly depolymerized by milling is dissolved in a suitable solvent (carbon tetrachloride or benzene) and then chlorinated. Additional depolymerization prior to chlorination may be effected by subjecting the solution to actinic light. Distillation removes the solvent and hydrogen chloride. The reaction product, which may contain 50 to 60 per cent of chlorine, forms fluid solutions which afford alkali- and acid-resistant lacquers or paints.

It has been said that chlorinated rubber prepared in the laboratory, besides being resistant to acids, alkalies, corrosive salts and strong oxidizing agents, is unaffected by ultraviolet light.[112]

In the preparation of chlorinated rubber [113] chlorine is introduced into solutions of rubber of a concentration of 2 per cent or less and of low viscosity, and the resulting rubber chloride solution is gradually poured into hot water in which is immersed a disintegrating apparatus whereby the solvent is evaporated and the chloride is reduced to the granular state. Prior to adding it to water, the solution may be reduced in viscosity by standing, exposure to light, or by the addition of alkali. The time for chlorination is also greatly reduced by irradiation.[114] Subsequent to chlorination, the product may be further irradiated (sunlight or mercury arc) until the desired viscosity is reached.

By the use of ultraviolet rays, Floresco [115] increases the concentration of rubber

[95] Porritt, B. D., and Dawson, T. R., British P. 269,745, May 25, 1926, to Research Association of British Rubber and Tyre Manufacturers; *Chem. Abs.*, **22**, 1498 (1928).

[96] Lister, W. N., *J. Soc. Chem. Ind.*, **46**, 220T (1927); see also Kelly, A., Taylor, B. S., and Jones, W. N., *Ind. Eng. Chem.*, **20**, 296 (1928).

[97] Poritt, B. D., Dawson, T. R., and Research Association of British Rubber and Tyre Mfrs. British P. 299,169. Sept. 29, 1927; *Brit. Chem. Abs.*, **B**, 937 (1928).

[98] Henri, V., *Caoutchouc & gutta-percha*, **7**, 4372 (1910); Matter in this paragraph is derived from Shepard, N., Krall, S., and Morris, H.[94]

[99] Bing, K., *Kolloid-Z.*, **4**, 232 (1909).

[100] Ditmar, R., *Gummi-Ztg.*, **21**, 243 (1906).

[101] Kreusler and Budde, German P. 18,740, Aug. 26, 1881.

[102] Himmelbauer and Co., *Chem. Ztg.*, **36**, 1441 (1912).

[103] Ahrens, F., *Chem. Ztg.*, **36**, 1441 (1912).

[104] Chertoff, G. J., U. S. P. 1,379,743, May 31, 1921; *Chem. Abs.*, **15**, 3414 (1921).

[105] Repony, D., *Rubber Age (N. Y.)*, **5**, 5 (1919).

[106] Mazurek, S., and Josse, Z., *Przemysl Chem.*, **18**, 481 (1934); *Brit. Chem. Abs.*, **B**, 144 (1935).

[107] Coe, M. R., U. S. P. 2,042,333; *Chem. Abs.*, **30**, 5071 (1936).

[108] Note also for the effects of other light filters, Margaritov, V., *J. Rubber Ind. (U.S.S.R.)*, No. 1, 42, 1936.

[109] Livings, G., and Lacey, B., British P. 418,035, 1934, to Dunlop Rubber Co., Ltd.; Canadian Patent 354,930; *Chem. Abs.*, **29**, 2395 (1935).

[110] Morse, D. S., U. S. P. 2,047,880, July 14, 1936; *Chem. Abs.*, **30**, 6240 (1936).

[111] Dyche-Teague, F. C., British P. 305,968, Sept. 13, 1927; *Brit. Chem. Abs.*, **B**, 334 (1929).

[112] Kojima, K., and Toyabe, Y., *J. Soc. Chem. Ind. Japan*, **36**, 236B (1933); *Chem. Abs.*, **27**, 3852 (1933).

[113] British P. 400,898, Nov. 2, 1933, to Chemische Fabrik Buckau; *Chem. Abs.*, **28**, 2219 (1934).

[114] French P. 768,157, Aug. 1, 1934, to Chemische Fabrik Buckau; *Chem. Abs.*, **29**, 640 (1935); Mollney, E., German P. 660,524, May 28, 1938; *Chem. Abs.*, **32**, 6905 (1938).

[115] Floresco, N., French P. 768,632, Aug. 10, 1934; *Chem. Abs.*, **29**, 640 (1935); Floresco, N., and Pfrunder, N., French P. 787,212, Sept. 19, 1935.

solutions to be halogenated without increasing their viscosities. The rays were said also to activate the halogenation and increase the stability of the products formed.

Buisov, Molodenskiĭ and Mikhaĭlov [116] stated that a chlorinated rubber containing 51.1 per cent of chlorine did not disintegrate in ten hours of exposure to ultraviolet rays. A freshly prepared rubber solution which had been irradiated for six hours gave after fifty minutes of chlorination a product with 68.2 per cent of chlorine. On the other hand, a solution of rubber containing 10 per cent of benzoyl peroxide after irradiation for eight hours and chlorination for one hour gave a product containing only 40.2 per cent of chlorine. This was unstable to light and heat. They conclude that the rubber must be disaggregated but not oxidized if it is to yield a good chlorinated product.[117] In discussing the use of chlorinated rubber in lacquers, Rosenthal and Schulze [118] state that because of the action of ultraviolet rays upon this product, only pigmented films are of practical use. They recommend titanium dioxide, chromium trioxide green, iron oxide pigments and graphite. Among other substances proposed [119] to be added in amounts up to 5 per cent to increase the light-stability of chlorinated rubber are dicyclohexylamine, ditetrahydrofurfurylamine, methyleneaminoacetonitrile, cyclohexylamine-formaldehyde, cyclohexylamine acetonitrile, tetramethylthiuramdisulfide, diphenylguanidine and dihydroxydiphenylpropane. Campbell and Reed [120] find 4-hydroxy-2-methyl-N-phenylmorpholine the best of six new N-phenylmorpholines in protecting rubber from staining after artificial illumination. Baxter [121] finds that plasticizers absorbing wave-lengths shorter than 3100A, such as dibutyl phthalate, stabilize chlorinated rubber and protect it from discoloration by light. Ethylene oxide is also recommended by Becker.[122]

Ultraviolet light is used by Laurin and Bidot [123] in the preparation of a substitute for rubber. To a mixture of glue as hydrogel with gum tragacanth and wood dust there are successively added: glycerol, vegetable oils, such as castor or colza oil, a resinate treated with formaldehyde, a resin solution such as a solution of Bakelite in naphtha, potassium dichromate, and potassium alum. Each addition is followed by a homogenization and the mass is kept in darkness from the time the potassium alum is added for a variable time subsequently. Pieces of the product obtained are exposed to ultraviolet rays to effect stabilization.

[116] Buisov, B. V., Molodenskiĭ, V. S., and Mikhaĭlov, N. I., *J. Rubber Ind. (U.S.S.R.)*, **11**, 44 (1934); *Chem. Abs.*, **29**, 953 (1935).

[117] For the action of ultraviolet on chlorinated rubber, see also *Synthetic and Applied Finishes*, 65 (1934).

[118] Rosenthal, L., and Schulze, G., *Farben-Chem.*, **5**, 53 (1934); *Brit. Chem. Abs.*, **B**, 636 (1934).

[119] British P. 437,304, Oct. 22, 1935, to Wingfoot Corp.; *Chem. Abs.*, **30**, 2422 (1936). British P. 479,464, Feb. 7, 1938; *Chem. Abs.*, **32**, 5256 (1938).

[120] Campbell, A. W., and Reed, M. C., *Ind. Eng. Chem.*, **28**, 656 (1936).

[121] Baxter, J. P., *Chemistry and Industry*, 407 (**1936**); *Chem. Abs.*, **31**, 4531 (1937).

[122] Becker, W., *Rubber Tech. Conf., London, Preprint* No. **96**, May, 1938; *Chem. Abs.*, **32**, 8192 (1938).

[123] Laurin, L., and Bidot, E., U. S. P. 1,969,932, Aug. 14, 1934; *Chem. Abs.*, **28**, 6348 (1934).

Chapter 32

Textiles, Paper and Dyestuffs

Coarse yarns are less affected by light than are fine ones, because in the former the outer layers protect the inner strands.[1] Of the various fibers, Barr found silk to be more affected by light than cotton, but wool much less than either. Artificial silk is affected less than cotton.

Simola [2] found that exposure to sunlight through a double glass window for five warm months reduced the tensile strength of cotton 17.8 and of wool 7.3 per cent. The stretching properties were reduced an average of 12 per cent for cotton yarn and 37.7 per cent for worsted yarn. Fine-fibered wool suffered more than coarse-fibered.[2a]

Expressed as the hours of sunshine required to cause a loss of 50 per cent in tensile strength, the order of deterioration of various textile fibers is as follows: silk (200), jute (400), artificial silk (900), cotton (940), flax (990), hemp (1100), raw wool (1120), chromed wool (1900). In this evaluation, the varying thicknesses of the textiles were not taken into account.[3]

Moisture, contrary to previous opinions, favors the deterioration, especially in the case of wool and bast fibers. The purer the atmosphere, the less is the destruction.

Waentig [4] found the tearing strength of wool practically unaffected by sunlight or by rays from a quartz mercury lamp, the washed fibers being slightly more sensitive than the raw wool. Carver [5] recommended ultraviolet radiations for testing fabrics used in automobiles.

It has been proposed to increase the resistance of textiles to ultraviolet light and water [6] by subjecting them to the successive action of a tanning solution containing a wetting agent (5 per cent catechu and 5 per cent Tetraconite, a mixture of Turkey red oil, pyridine and tetrachloroethane), a mordanting solution (5 per cent lead acetate) and an oiling solution containing an aldehyde or ketone (5 per cent linseed oil in tetrahydronaphthalene with 2 per cent paraldehyde) to control the rate of oxidation during drying.

Cotton and Cellulose. Little is yet known as to the wave-lengths which are required for the destruction of cotton or cellulose. Barr [7] maintained it to be

[1] Barr, G., *Trans. Faraday Soc.*, **30**, 284 (1924); Waentig, P., *Z. angew. Chem.*, **36**, 357 (1923).

[2] Simola, E. J., *Teknillinen Aikakauslehti*, **23**, 326 (1933); *Chem. Abs.*, **28**, 647 (1934); *Acta Fennica*, **6A**, 126 (1933).

[2a] Mercerized cotton lost 13.7 per cent in tensile strength and 27.3 per cent in elasticity.

[3] Sommer, H., *Chem. Ztg.*, **51**, 777 (1927). Later, with Heermann, P., *Leipzig Monats. Textilind.*, **40**, 207 (1925) the order is given as: mineral weighted silk, raw silk, jute, raw and bleached cotton, raw wool, mercerized cotton, nitro- and viscose rayons, chromed wool, bleached flax yarn, cuprammonium rayon, raw flax yarn.

[4] Waentig, P., *Z. angew. Chem.*, **36**, 357 (1923). See also *J. Soc. Chem. Ind.*, **39**, 512A (1920); Vignon, L., *Ibid.*, 482A; **42**, 825A (1923).

[5] Carver, W. L., *Automotive Industries*, May 8, 1011 (1924).

[6] British P. 263,102, Nov. 4, 1926, to Albert Meyer-Sans Boeuf Co.; *Brit. Chem. Abs.*, **1927B**, 746.

[7] Barr, G., *Trans. Faraday Soc.*, **20**, 284 (1924).

[8] Kauffmann, H., *Textilber.*, **7**, 617 (1926); *Chem. Abs.*, **20**, 3352 (1926).

due chiefly to wave-lengths shorter than 4000A. Kauffmann[8] finds the region about 3500A probably effective, and states that visible light is without action.

Notwithstanding a considerable amount of work, the question as to whether an oxidation is involved cannot yet be said to have been definitely settled. Dyer and Dorée,[9] who reviewed some of the earlier observations, concluded that ultraviolet rays convert cellulose into oxycellulose with complete loss of tensile strength, a view shared by Barr,[10] and by Aston.[11]

A new point of view was introduced by Kauffmann,[12] who believed the deterioration to occur independently of the presence of oxygen and without any change in weight. He concluded that the recognized formation of oxycellulose is preceded by the production of a compound "photocellulose," the formation of which does not involve oxidation. Like oxycellulose, the "photocellulose" reduces silver salts or Fehling's solution and shows a yellow color with caustic soda and phenylhydrazine. It is soluble in sodium hydroxide solution and has the formula $C_6H_{10}O_5$.

The action of ultraviolet light during the sun bleaching of cotton leads to the production of "photocellulose," the formation of which can be followed by a method involving the use of potassium permanganate. In cotton fabrics exposed for 45 days, 1 to 2 per cent of "photocellulose" is produced. The observed increased affinity of the exposed cotton for methylene blue was not, however, ascribed by Kauffmann to the presence of "photocellulose." This view is accepted by Sommer.[13]

Barr and Hadfield,[14] however, concluded that an oxidation is involved. No significant change took place when strips of cotton cloth were exposed for six months to sunlight in sealed glass tubes containing hydrogen or about two-thirds saturated with water vapor. Similar exposure in tubes containing oxygen resulted in a considerable loss of strength, an increase in reducing power as shown by the copper number, and the production of carbon dioxide and carbon monoxide and perhaps hydrogen. The reaction was more rapid in the presence of moisture. There was a rough parallelism between the copper number and the quantity of carbon dioxide produced. With increase in the time of exposure, there was a continuous decrease in strength and of the viscosity of cuprammonium solutions prepared from the exposed cotton. The methylene blue absorption by the cotton showed first a fall and then a slow rise. In general, the modification of cotton produced by the light corresponded to that formed by mild oxidation with chlorine water. Cotton cloth previously steeped in 0.001*N* sulfuric acid is more highly reducing and shows a greater production of carbon dioxide under the same conditions of exposure. Precipitation of ferric hydroxide on the cotton before exposure results in an increased attack by the light, but lessens the formation of carbon dioxide.

These workers recognized, however, that at least two reactions may occur during the exposure of cotton to sunlight. Both are accompanied by a loss of strength and the development of reducing power. One reaction, however, produces much less carbon dioxide than the other, and is catalyzed by iron.

[9] Dyer, J., and Dorée, C., *J. Soc. Dyers Colourists*, **33**, 17 (1917); *Chem. Abs.*, **11**, 1753 (1917). See also Scheurer, A., *Bull. Soc. Mulhouse*, **80**, 324 (1912). A recent review is given by Cady, W. H., *Am. Dyestuff Rept.*, **27** *(Proc. Am. Assoc. Textile Chem. Colorists)*, p. 325 (1938); *Chem. Abs.*, **32**, 5632 (1938).

[10] Barr, G., *Trans. Faraday Soc.*, **20**, 284 (1924).

[11] Aston, F. W., Report on the Action of Sunlight on Aeroplane Fabrics T1019, British Advisory Committee for Aeronautics, 1917.

[12] Kauffmann, H., *Textilber.*, **7**, 617 (1926); *J. Soc. Chem. Ind.*, 817 (1926); *Chem. Abs.*, **20**, 3352 (1926).

[13] Sommer, H., *Chem. Ztg.*, **51**, 777 (1927).

[14] Barr, G., and Hadfield, I. H., *J. Textile Inst., Special Issue*, **18**, 490 (1927); *Chem. Abs.*, **22**, 2062 (1928).

The deterioration of linen also appeared to be the result of oxidation. Loss of strength occurred most rapidly in oxygen, less so in air, and was negligible in hydrogen, carbon dioxide or a vacuum.

According to Sharvin and Pakshver,[15] exposure of bleached, ether-extracted, washed and dried cotton in sealed tubes with oxygen to sunlight showed a simultaneous formation of oxycellulose, carbon dioxide and water. During the earlier part of the process, there seemed to be a definite relation between the amounts of carbon dioxide and of oxycellulose formed, although it could not be expressed stoichiometrically. Upon continued exposure, the carbon dioxide formation decreased, but the oxycellulose appeared to undergo a further oxidation. In addition to the formation of carbon dioxide and water, there were produced compounds which had the odor of furfural but did not give its reactions. The fabric lost both in strength and in weight.

Ditz[16] concludes that more work is necessary to explain the mechanism of the degradation of cellulose, an especially important reaction in the "grass-bleaching" of fabrics. Dumas[17] reviews the analytical methods employed in such investigations.

It has recently been noted[18] that the sorption of iodine from the vapor phase by cotton is greater after the cotton has been irradiated by ultraviolet light. Williams[19] observed that cotton or viscose yarns when deteriorated by excessive bleaching or ultraviolet irradiation, lose much of their remaining strength, when wet. The ratio between wet strength and air-dry strength appeared to be a function of the degree of deterioration.

When exposed to the quartz mercury-vapor lamp, cotton hairs lose strength at a constant rate until the tendering amounts to about 40 per cent; the rate then diminishes.[20] Over a small range, the rate of tendering is proportional to the intensity of the light. Cotton hairs of different origin exhibit specific differences in their susceptibility to light tendering. The proportional loss of strength of yarns is about half that of hairs fully exposed under the same conditions, the hairs in the yarns being tendered to the same extent as the yarns. Bleached cotton is more rapidly tendered than raw. Material dyed with chrome green is much more resistant than the undyed scoured material. Ferric hydroxide has a slight protective action. Cloth-dyed mineral khaki is as resistant as the chrome-dyed material, the effect being such as to extend the life of fabrics subject to strong illumination to as much as five or six times that of untreated materials. Organic dyes modify the rate of tendering of cotton by light, some favorably and others unfavorably, but the effect is never as large as that of chromium hydroxide.

Experiments conducted for the British Government indicated[21] that heavy cotton and linen tent fabrics are much less affected by sunlight than are the light and less exposed fabrics used in airplane and airship construction. Although such pigments as lead chromate diminish the deterioration by light, others, such as the stannates, tungstates and sulfides frequently used in fire proofing, accelerate it. Waterproofing frequently, but not always, has a beneficial action, depending on the process and materials used, the climatic conditions and the exposure.

[15] Sharvin, V. V., and Pakshver, A., *Z. angew. Chem.*, **41**, 1159 (1928); *Chem. Abs.*, **23**, 3080 (1929).

[16] Ditz, H., *Z. angew. Chem.*, **40**, 1476 (1927).

[17] Dumas, M. J., *Rev. gen. mat. color.*, **41**, 149 (1937).

[18] Beutel, E., and Kutzelnigg, A., *Monatsh.*, **64**, 41 (1934); *Chem. Abs.*, **28**, 3591 (1934).

[19] Williams, J. G., *J. Soc. Dyers Colourists*, **48**, 167 (1932); *Chem. Abs.*, **26**, 4477 (1932).

[20] Cunliffe, P. W., Farrow, F. D., and Midgley, E., *J. Textile Inst.*, **19**, 169T (1928); *Brit. Chem. Abs.*, **B**, 563 (1928).

[21] Hunter, J. A., *Textile World*, **69**, 309, 315 (1926); *Chem. Abs.*, **20**, 827 (1926).

After 500 hours in sunlight, 35 white and dyed cotton fabrics tested by Grimes[22] showed losses in breaking strength of 18 to 49 per cent in the warp and 34 to 65 per cent in the filling. The mercerization of the Everfast suitings and broadcloths tested increased their resistance to tendering. In eight of fifteen dyed fabrics tested, less breaking strength was lost than in undyed fabrics. The time of exposure had far more effect on the loss of strength than had the temperature and relative humidity. Spectrophotometric analysis showed that sunlight affected the color of all white and dyed fabrics tested. The white ones became increasingly yellow with increased exposures.

The resistance of "tobacco cloth" to sun and rain may be improved by letting an acidulated solution of lead acetate penetrate it and then treating it with a solution of sodium dichromate so as to form lead chromate on the fibers.[23]

Anthracene yellow GC and Chrysoidine have been found unsatisfactory for the protection of cotton from deterioration by light.[24]

Cotton and viscose silk materials dyed with one of a large number of orange and yellow vat dyes (Indanthrene Yellow G and Alizanthrene Yellow 6R excepted) if exposed to light and air immediately after dyeing while the dye is in its leuco condition, become tendered by oxidation.[25] The dye itself may also be simultaneously oxidized, with consequent partial or complete decolorization. If a second dye is present (especially Ciba Blue 2B), this may be oxidized in preference to the cotton or the first dye. These effects also are produced when the dyed fabric is oxidized in darkness before exposure to sunlight or a Fade-Ometer, but are not produced if again washed before exposure. Tendering occurs if the washed fabric is further impregnated with a dilute solution of caustic soda containing sodium hyposulfite or hydrogen peroxide and then exposed to light and air. By means of the starch iodide test it was shown that an active oxidizing agent, probably hydrogen peroxide, was formed during the oxidation of cotton dyed with Cibanone Yellow R. Certain direct dyes, including Diamine Fast Yellow and Chlorazol Fast Orange R, behave similarly to vat dyes in promoting tendering. The tendering of cotton when so exposed is rapid and may be serious in large-scale dyeing. For example, cotton fabrics lifted successively five times (ten minute exposure each time) from the dye liquor and exposed to light and air while being dyed with 20-per cent Cibanone Orange R had copper numbers of 0.2, (original fabric), 0.3, (dyed fabric not exposed), and 0.7, 1.3, 1.5, 1.7 and 1.75 (after five successive exposures). Viscose silk is particularly susceptible to tendering under these conditions. The destructive action of sunlight is not appreciably affected by transmission through plate glass a quarter of an inch thick or didymium glass opaque to yellow light.

A fading product of Ciba Blue 2B dyed on cotton, isolated by Scholefield, Hibbert and Patel,[26] appeared to be dibromoisatin. The fading products from cotton dyed with methylindigo gave the reactions of *o*-methylisatin. Hibbert[27] also impregnated calico, wool and cellulose acetate silks with 1,2,4-trihydroxyanthraquinone Purpurin. After 60 hours of exposure to the Fade-Ometer, a substance was extracted by carbon tetrachloride which was found to be a mixture of phthalic acid and phthalic anhydride. Impregnation of calico with phthalic acid and its anhydride followed by exposure to the Fade-Ometer and extraction with alcohol and carbon tetrachloride was found to increase its affinity for methylene blue. Tables showing the manner in which various dyes catalyze the tendering action of sunlight on cotton have been given by Vashist.[28]

Haller and Wyszewianski[29] investigated the sensitization of the photodecomposition of cotton by a series of vat dyes by exposing 25 per cent[30] dyeings on 10 gm. of heavy cotton calico to sunlight at a 45° angle to the south under 2 mm. of Ultravit glass. The loss of tensile strength was 9 per cent in white bleached calico after 130 normal bleaching hours. When treated with various anthraquinone intermediates, the corresponding losses were: anthraquinone, 27 per cent; 2-methylanthraquinone, 46 per cent; 1-chloroanthraquinone, 32 per cent; 2-chloroanthraquinone, 41 per cent; 1-aminoanthraquinone, 17 per cent; 2-aminoanthraquinone, 18 per cent; anthraquinone-1-sulfonic acid, 13 per cent and anthraquinone-2-sulfonic acid, 20 per cent; anthraquinone-1,5-disulfonic acid, 24 per cent. Graphs showed a decrease of as much as 40 per cent in the tear strength of cotton dyed with certain anthraquinone dyes after only 79 normal bleach hours, the dyeings varying from 0.05 to 1.0 per cent. Henk[31] believes that in such cases the deterioration involves oxidation. It depends on the temperature, fiber structure and the presence of hydroxyl, amino or imino groups. The destructive process is hastened by such catalysts as the metal compounds in sizes and after-treatment, particularly chromium and copper salts, impure water containing manganese and nickel, and the titanium dioxide used in the manufacture of delustered rayons.

A method of producing light and elastic threads or cellulose cloths consists in impregnating them with the chlorates, bromates or iodates of metals of the second periodic group. These, under the influence of photoactive rays (but not ordinary light) degrade the fibers.[32]

Pacini[33] has made the claim that the tensile strength of cellulosic materials such as cotton may be actually increased by subjecting it to ultraviolet radiation controlled in a special manner to prevent the formation of detectable oxycellulose.[34]

Paper and Wood Pulp.[35] The bleaching of wood pulp, paper products or cotton textiles by chlorine is accelerated both by light and by increased temperatures. It is usually cheapest to depend upon the thermal reaction alone, but in certain cold climates where fuel is expensive, attempts have been made to employ artificially produced ultraviolet light for aiding the process. Escourrou[36] investigated the accelerating effect of a mercury-vapor lamp. Although the process could be carried out at a lower temperature, more chlorine was used, owing to the

[22] Grimes, M. A., *Texas Agr. Sta., Bull.* **506,** 5 (1935); *Chem. Abs.*, **30,** 291 (1936).

[23] Rhodes, G. H., U. S. P. 2,026,190; *Chem. Abs.*, **30,** 1247 (1936).

[24] Kauffmann, H., *Textileber*, **7,** 617 (1926); *Brit. Chem. Abs.*, **1926B,** 817.

[25] Scholefield, F., and Patel, C. K., *J. Soc. Dyers Colourists*, **44,** 268 (1928); *Brit. Chem. Abs.*, **B,** 811 (1928); *J. Soc. Dyers Colourists*, **45,** 175 (1929); *Chem. Abs.*, **23,** 4824 (1929).

[26] Scholefield, F., Hibbert, E., and Patel, C. K., *J. Soc. Dyers Colourists*, **44,** 236 (1928); *Chem. Abs.*, **22,** 3780 (1928).

[27] Hibbert, E., *J. Soc. Dyers Colourists*, **45,** 204 (1929); *Chem. Abs.*, **23,** 4824 (1929).

[28] Vashist, S. D., *Indian Textile J.*, **42,** 376 (1932); *Chem. Abs.*, **27,** 192 (1933).

[29] Haller, R., and Wyszewianski, L., *Melliand. Textilber.*, **17,** 45, 138, 217, 325 (1936); *Chem. Abs.*, **30,** 6566 (1936).

[30] Wahl, A., [*Rev. gen. mat. color.*, **38,** 217 (1934); *Chem. Abs.*, **28,** 4910 (1934)] links the destructive action of the dyes with an absorption band at about 3300 to 3700 Å.

[31] Henk, H. J., *Monatschr. Textilind.*, **51,** 186 (1936); see also E. Baur, *Helv. Chim. Acta.*, **20,** 879 (1937).

[32] French P. 803,145, Sept. 23, 1936, to Comptoir des textiles artificiel; *Chem. Abs.*, **31,** 2837 (1937).

[33] Pacini, A. J., U. S. P. 1,948,276, Feb. 20, 1934, to Millprint Products Corp.; *Brit. Chem. Abs.*, **B,** 1053 (1934).

[34] For the absorption of cellulose films in the extreme ultraviolet (800A.), see O'Bryan, H. M., *J. Opt. Soc. Am.*, **22,** 739 (1932). It has been shown that the change in absorption of alkali cellulose during xanthogenation may afford a method for following the progress of the process. Atsuki, K., and Sobue, H., *J. Soc. Chem. Ind. Japan*, **36,** Suppl. binding, 589 (1933); *Chem. Abs.*, **28,** 710 (1934).

[35] Data on the absorption spectrum of lignin have been given by Herzog, R., and Hilmer, A., *Ber.*, **64B,** 1288 (1931); *Papier Fabr. Tech. Wiss. Teil*, **30,** 205 (1932); **29,** 4-5; *Chem. Abs.*, **26,** 4309 (1932); Hilmer, A., *Ber.*, **66B,** 1600 (1933); Hägglund, E., and Klingstedt, F. W., *Z. physik. Chem.*, **152A,** 295 (1931); Stamm, A. J., Semb, J., and Harris, E., *J. Phys. Chem.*, **36,** 1574 (1932).

[36] Escourrou, R., *Chimie et industrie*, **19,** 989 (1928); *Brit. Chem. Abs.*, **B,** 168 (1929); *Pulp Paper Mag. Canada*, **26,** 1549 (1928); *Chem. Abs.*, **22,** 4791 (1928).

increased formation of chlorates which play no part in bleaching. Furthermore, the cellulose, as well as the non-cellulose impurities in the wood pulp paste, was attacked. The material thus obtained was rich in oxy- and hydro-cellulose, as shown by its enhanced copper number. The α-cellulose content fell and the β- and γ-cellulose content rose. Although this is not important in paper-making, it is a disadvantage when the material is to be employed for making viscose and certain kinds of cellulose nitrate. This effect is observed only when chlorine bleaching agents are used, but not with ozone or hydrogen peroxide. In knot-pulp, the use of ultraviolet light in conjunction with hypochlorite bleaching did not exert a deleterious action, presumably because the chlorine reacts more readily with the ligneous constituents than with cellulose.

According to Edge and McKenzie,[37] light causes two changes in paper pulp, a yellowing and a fading or whitening. Sunlight causes a definite yellowing in three hours, and whitening only after about two weeks. The latter effect may be due to a bleaching of pulp constituents not removed in ordinary bleaching. Discoloration is more rapid at 90 per cent than at 30 per cent relative humidity, and is great for samples exposed to the sun's heat while shielded from its light. Yellowing by a mercury arc varies with the age of the lamp.

Wahlberg[38] believed illumination to effect a saving of bleaching liquor and of steam about equal to the cost of the light, but found application difficult because the light affects only the surface. Hirschkind, Pye and Thompson[39] obtain good results with a mercury arc, provided rays shorter than 3000A are removed since these are harmful to cellulose. Wave-lengths longer than 4000A are ineffective. The best range is 3500A[40] to 3850A.

Attempts at standardizing the test for the light-resistance of various fibrous paper-making materials have been made by Kovalevskii.[41] An ordinary carbon arc produced after 80 to 100 hours changes in the resistance to breaking of paper and fiberboard that were too slight to be of use in the rapid laboratory testing of these substances. However, a Sperry carbon arc (150 amps., 79 volts, 950,000 c.p.) gave satisfactory results in exposures of twenty hours at 1.3 meters, in the case of sheets from unbleached sulfite pulp, sulfate kraft, straw pulp, mechanical wood pulp, linen rags, cotton, spruce, jute and a mixture of 60 per cent wool and 40 per cent kraft. All materials showed a decrease of 15 to 59.5 per cent in the resistance to breaking, with unbleached sulfite the most and jute and the two straw stocks the least affected. This contradicted a prevalent idea of the excessive destructibility of materials derived from lignified fibers. The stretching power of raw materials was impaired, but to a lesser degree than the resistance to breaking. Mechanical wood pulp and wool showed an increase in the stretching ability. The tests showed that in the process of aging by heat and light, all grades of paper undergo an insignificant change in their tearing length, and that this factor is less characteristic of the physical changes than is the resistance to breaking. The sorption of anthracene oil on raw materials was but little affected, except that that of wood pulp and wool was slightly improved.

The reflection of ultraviolet light by paper is not very different from that of

[37] Edge, S. R. H., and McKenzie, H. M., *Proc. Tech. Sect. Paper Makers' Assoc. Gr. Brit., Ireland*, **17**, Pt. 2, 437 (1937); *Chem. Abs.*, **31**, 4113 (1937); Bakker, H., *Chem. Weekblad*, **34**, 543 (1937); *Chem. Abs.*, **32**, 3958 (1932).

[38] Wahlberg, H. E., *Ind. Pappers Tid.*, **38**, 481 (1934); *Chem. Abs.*, **28**, 7008 (1934).

[39] Hirschkind, W., Pye, D. J., and Thompson, E. G., *Paper Trade J.*, **105**, TAPPI Sect. 268 (1937); *Brit. Chem. Abs.*, **B**, 147 (1938).

[40] Hirschkind, W., Pye, D. J., and Thompson, E. G., *Paper Trade J.*, **105**, No. 18, 118 (1937); *Chem. Abs.*, **32**, 772 (1938).

[41] Kovalevskii, I. I., *Bumazhnaya Prom.*, **14**, No. 2, 13 (1935); *Chem. Abs.*, **29**, 5264 (1935).

ordinary light.[42] Papers water- and oil-proofed by vinyl resins are more readily penetrated by ultraviolet light than ordinary paper.[43] When paper containing resins is exposed to the sun, it tends to become yellow and soluble in cold weak alkalies or water.[44] The results may differ when artificial ultraviolet light sources are employed and these should be used only in the absence of sunlight. Bleached and unbleached rosin darkens in light,[45] and ferrous resinates and rosin size, if contaminated with ferrous iron, are also light-sensitive. Ferric resinates, aluminum resinate and sodium resinate have no ability to cause yellowing of paper in light.

Oguri,[46] in giving data on the increase in the copper number of filter paper, tissue paper and viscose rayons which follows exposure of these products to the rays of a quartz mercury arc, attributed it to the action of ozone formed by the lamp. Aldehydes appeared to be formed even in the absence of oxygen. Bromley[47] noted that when pulp-sized paper of good quality and free from resin is irradiated by the mercury arc, it rapidly loses its property of ink resistance, and the surface color degrades to a brown shade. He believed the browning to be a function of the gelatin present, which he found to be degraded to simpler products.

Most studies of the deterioration of paper by light have been made in sunlight. Richter[48] found that after 50 to 100 hours, the sacrifice in tear strength and tensile strength was in general slight in comparison with the loss in folding endurance, even though the fold strength of the sample tested had been originally greatly enhanced by the application of glue. Rosin- and starch-sized papers were at least as sensitive to loss in writing qualities as were glue-sized papers. The protective effect of glass was marked in the case of papers made from purified wood fiber and sulfite papers were partly protected, but newsprint deteriorated as rapidly under glass as when exposed directly. When purified wood fiber papers under glass in hydrogen were exposed to sunlight, there was apparently no degradation. Sulfite papers under these conditions showed a loss in fold strength, although the copper number did not increase. When similar papers were exposed under glass with oxygen, they retained 78 and 38 per cent, respectively, of their original fold strengths. Changes in the copper number were in the same order. When air was substituted for oxygen, the fold strength retentions were 90 and 58 per cent, respectively. Neutral mineral oil coatings did not protect papers from oxidation in sunlight. A glycerolated paper was somewhat less sensitive. Surface sizing with various waxes and starch caused no improvement and rosin was definitely harmful. A coating of regenerated cellulose, prepared by means of properly applied viscose solutions, was advantageous both for fold strength and for fold retention. Sodium stannate appeared to have a protective action but deterioration was hastened by the presence of sodium molybdate or of iron compounds, at least in a water-leaf purified wood-fiber sheet. Water-leaf papers lose from one to two per cent in weight when exposed a hundred hours on each side. In wood veneer strips, the changes in copper number are very great and in the case of poplar wood a marked delignification takes place.

[42] Déribéré, M., *Papier*, **38**, 1083 (1935); *Chem. Abs.*, **30**, 2379 (1936).

[43] Ohl, F., *Wochlbl. Papier-Fabr.*, **67**, 5 (1936); *Chem. Abs.*, **30**, 2755 (1936); see also Chinchin, I., *Bumazhnia Prom.*, No. 12 (1924); **14**, 12 (1935).

[44] Marini, M., *Bol. staz. sper. Carta*, **6**, 16 (1927); *Chem. Abs.*, **21**, 2188 (1927).

[45] Kimberly, A. E., and Hicks, J. F. G., *Bureau Standards J. Research*, **6**, 819 (1931).

[46] Oguri, S., *J. Soc. Chem. Ind. Japan*, **37**, 620B (1934); *Chem. Abs.*, **29**, 1241 (1935); for the effects of various surrounding oxygen concentrations, see Oguri, S., and Yamaguchi, T., *J. Soc. Chem. Ind. Japan*, **40**, 300B (1937). Oguri, S., and Takei, M., [*J. Soc. Chem. Ind.*, **41**, 3 (1938)] find only wave-lengths less than about 3640A effective.

[47] Bromley, H. A., *Analyst*, **58**, 29 (1933).

[48] Richter, G. A., *Ind. Eng. Chem.*, **27**, 177, 432 (1935).

Red, green, lemon-yellow, dark brown-yellow and light brown-yellow window glasses each afforded some protection when papers (double-sized rag, rosin-sized papers from 50 per cent rag and 50 per cent sulfite pulp and pure sulfite paper) were exposed to direct sunlight for 523 hours or to diffused sunlight for 767 hours. The degree of protection depended upon the extent to which the filters removed the shorter wave-lengths, the range between 4600 and 4000A being strongly injurious. The yellow, green, and red glasses afforded practically the same protection.[49] The brown-yellow glasses gave the least protection, since both of them transmitted some wave-lengths down to about 3300A.

Blaisdell and Minor [50] studied the aging properties of a very white facial tissue made of highly bleached wood fiber and of a cream-colored toweling of underbleached sulfite wood fiber, by determining the copper number and absorbent properties before and after exposure for one hour to a Victor ultraviolet lamp at a distance of ten inches at 38°C. The original copper numbers of papers of this type gave no clue as to their permanence. A large change in this test may be considered as indicative of a rapid loss of absorbent properties on normal aging.

A method advocated by Wright [51] for waterproofing paper consists in impregnating it with a solution of gelatin, casein, or similar protein, and bichromate of potassium or sodium. On exposure to the rays of a quartz mercury arc, the protein becomes insoluble and the paper is strengthened and made waterproof. The solution may also be added to paper pulp and the irradiation carried out after sheeting.

Ruderman [52] coats paper with a suspension of dry starch and sulfur in cold water and then exposes it to ultraviolet light.

Considerable application has been made of fluorescence in filtered ultraviolet light in the analysis of papers and paper-making materials but the discussion of this topic lies beyond the scope of this book.[53] Testi [54] states that with rays of 3000 to 4000A, sulfite cellulose yields a color not caused by lignin, sulfur or lignosulfurous materials, but by an unknown principle in wood and its bark which resists various chemical treatments. White papers containing cotton, linen and hemp fibers assume a light-yellow color, and paper from chemical cellulose a white color with slight yellow tinge, and paper prepared chiefly from mechanical wood pulp, an intense violet color.

In testing the water resistance of paper by a method of this type, Grant [55] grinds 100 gm. of icing sugar, dried at 100°C., in a mortar with 0.5 gm. of Rhodamine 6G and sprinkles it from a bottle through 70-mesh bronze gauze on the specimen (2 sq. in.) floated on distilled water at 21°C. The time is taken with a stop-watch until, in a dark room, the upper surface of the paper irradiated with filtered ultraviolet first exhibits a bright golden fluorescence. This means that the water has just penetrated the paper, causing solution of the dyestuff.

Artificial Silk. Grempe [56] states that in the weathering of rayon and silk fabrics, the destruction takes place on the surface exposed to the light. It is due to both water and the ultraviolet rays of the sun. These fabrics lasted for about half a year when exposed to the weather. Huezel [57] has given curves showing the effect of exposure to ultraviolet light on the strength of textile fabrics prepared

[49] Köhler, S., *Tek. Tid. Uppl. C Kemi,* **65,** 49 (1935); *Chem. Abs.,* **29,** 6379 (1935).

[50] Blaisdell, C. A., and Minor, J. E., *Paper Ind.,* **15,** 512 (1933); *Chem. Abs.,* **28,** 2525 (1934).

[51] Wright, W. L., U. S. P. 1,542,539, June 16, 1925; *Brit. Chem. Abs.,* **B,** 627 (1925).

[52] Ruderman, A., U. S. P. 1,723,581, Aug. 6, 1929; *Chem. Abs.,* **23,** 4573 (1929).

[53] For general discussions, see Déribéré, M., *Papier,* **38,** 637 (1935); *Chem. Abs.,* **29,** 7652 (1935); Grant, J., *World's Paper Trade Rev.,* **103,** 1463, 1506, 1508, 1550, 1588, 1666 (1935); *Chem. Abs.,* **29,** 5266 (1935); Lewis, S. J., *J. Soc. Chem. Ind.,* **41,** 99R (1922).

[54] Testi, G., *Raggi ultravioletti,* 297, 1926; *Chem. Abs.,* **22,** 1472 (1928).

[55] Grant, J., *J. Soc. Chem. Ind.,* **53,** 349T (1934); see also Noll, A., and Preiss, K., *Papier-Fabr.,* **35,** Tech. Tl., 213 (1937); *Chem. Abs.,* **31,** 7248 (1937).

[56] Grempe, P. M., *Kunst-Seide,* **9,** 462 (1927); *Chem. Abs.,* **22,** 2469 (1928).

[57] Huezel, P., *Rayon and Melliand Textile Monthly,* **16,** 161 (1935); *Chem. Abs.,* **29,** 3170 (1935).

from viscose. The damage to viscose rayon is slightly greater in an atmosphere of 45 per cent relative humidity than in one of 65 or 90 per cent.[58] Acetate rayon deteriorates less than natural silk or other types of rayons.[59] Among various protective agents tested, β-methylumbelliferone and tannic acid were the most effective when test pieces were exposed to daylight through 3 mm. of ordinary window glass for 250 hours. Other protective agents, Tannigen FC, zinc salicylate and maleic acid, were found better when the acetate rayon was exposed to daylight through Uviol glass. Quercitin was best when the samples were exposed to the light of a mercury arc. The protective agents were used in 2 per cent solution, 1 per cent being usually taken up by the fiber. Eichler gave the following results for the deterioration of various products. The first number is the percentage decrease in tensile strength resulting from six hours of exposure to the mercury vapor lamp and the second that after exposure of 250 hours to daylight through window glass; natural silk, 28, 62; cuprammonium rayon, 11, 57; viscose rayon, 4, 35; acetate rayon, 35, 24; acetate rayon dyed black, 0, 1.2; acetate rayon dyed blue, 11, 17; acetate rayon dyed brown, 11, 13; unbleached cotton, 0, 0.

In the preparation of a selvedge-resistant material, Malm and Fordyce [60] form a sheet containing an ester of cellulose having an unsaturated acyl group such as cellulose tricrotonate and polymerize it by intense ultraviolet light for about five hours, or heat it to 100°C. for at least 24 hours.

The solubility properties of organic derivatives of cellulose may be modified by treatment with ultraviolet rays in the absence of oxygen.[61]

Silk. The photochemical destruction of this fabric depends upon the pH at which the exposures are made.[62] The maximum stability to the light of a glass-enclosed carbon arc is at about pH 10, the pH being measured in the aqueous extract of the sample. Above pH 11 and below pH 3, the stability decreases rapidly. In the intervening range, a minimum exists in the neutral region, indicating that the protein salts formed with small quantities of acid or alkali are more stable than the pure protein.

During the deterioration of silk in sunlight or north skylight, the ammonia nitrogen content is increased, as a result of oxygen attacking the silk under the influence of light.[63] Saito [64] found that exposure of silk fabrics to direct sunlight for 49 days gave a loss of 95.3 per cent of their tensile strengths. Against this, coatings of antioxidants had little effect.

X-ray diagrams of unweighted silk appeared similar before and after exposure to an S-1 sunlamp, but photometric analysis indicated a decrease in fiber orientation, causing the long fiber arc to expand toward the character of a powder pattern.[65] Lead-weighted silk underwent the greatest deterioration.[66] Pure-dye and 25 per cent tin-weighted samples slightly increased in tensile strength when

[58] Negishi, M., Umesawa, H., and Mori, H., *Rayon World,* **5,** No. 7, 1 (1937); *Chem. Abs.,* **32,** 4343 (1938).

[59] Eichler, A., *Melliand Textilber.,* **16,** 429 (1935); *Chem. Abs.,* **29,** 7084 (1935).

[60] Malm, C. J., and Fordyce, C. R., U. S. P. 1,973,493, Nov. 9, 1934, to Eastman Kodak Co.; *Brit. Chem. Abs.,* **B,** 737 (1935).

[61] Bincer, H., German P. 601,478, Aug. 16, 1934, to I. G. Farbenind. A.-G.; *Chem. Abs.,* **28,** 7527 (1934).

[62] Harris, M., and Jessup, D. A., *Bureau Standards J. Res.,* **7,** 1179 (1931); *Am. Dyestuff Reporter,* 20, 795; **23,** 215 (1934). *Cf.* Trotman, S. R., *J. Soc. Chem. Ind.,* **55,** 325T (1936).

[63] Harris, M., *Textile Mfg.,* **60,** 420 (1934); *Chem. Abs.,* **29,** 4589 (1935); *J. Bur. Stands. J. Res.,* 13, 151 (1934); *Am. Dyestuff Rept.,* **23,** 215 (1934); *Chem. Abs.,* **28,** 5675 (1934); Columbo, G., *Boll. ufficiale staz. sper. seta,* **4,** 73 (1934); *Chem. Abs.,* **31,** 8204 (1937).

[64] Saito, S., *J. Soc. Rubber Ind. Japan,* **7,** 92 (1934); *Chem. Abs.,* **28,** 3591 (1934).

[65] Bruner, E., and Goehring, M., *Textile Research,* **5,** 231 (1935); *Chem. Abs.,* **29,** 4948 (1935).

[66] Hess, K., and Bruner, E., *Kansas Agr. Expt. Sta. Rept.,* 120 (1934); *Chem. Abs.,* **30,** 2765 (1936).

exposed to wave-lengths longer than 3400A, but 50 per cent tin-weighted silk showed little or no change under these rays. All samples showed the greatest deterioration when exposed to wave-lengths between 2600 and 3400A, or to the entire spectrum. In dyed silks, color fastness was not in general sufficient to withstand Kansas sunshine, although only one sample in thirteen faded by the Fade-Ometer test.[67]

Sericin solutions are cleared and reduced in viscosity by ultraviolet light.[68]

Wool. Exposed wool no longer gives the von Allwörden reaction.[69] Meunier and Rey [70] observed that neutral wool develops a rose-violet color when treated with the vapor or solution of quinone, but a deep brown if previously exposed to sunlight or ultraviolet rays, the wool becoming more acid. This sharp difference may be utilized for the production of photographic prints on woolen fabrics. The effect of the irradiation is not dependent upon the nature of the surrounding atmosphere.

The superficial erosion of woolen cloth exposed to the air is ascribed by Heermann to the action of ultraviolet rays (2000-3500A).[71] After exposure to sunlight, wool swells strongly in dilute alkali and crumples in a characteristic manner.[72] After such exposure, it is dyed more deeply by basic dyestuffs and less so by acid dyes. Those dyes which yielded darker shades on wool which had been affected by sunlight than on unexposed wool were called positive. Those which yielded lighter shades after exposure were called negative. The positive or negative behavior of a dye toward wool usually increased with the duration of the exposure of the wool, but after a direct exposure of about 300 hours which almost completely destroyed the epithelial scales of the wool, the effect diminished. Indigo is positive after the wool has been exposed 100 hours, but after 264 hours, it is strongly negative. The behavior of acid dyes on exposed wool varies according to the acidity or neutrality of the bath from which they are applied. Alizarin Cyanin Green G is negative when applied from a neutral bath or one containing 3 per cent of acetic acid, but is strongly positive when applied from a bath acidified with 2 per cent of sulfuric acid. The differences in the behavior of dyes toward exposed wool are very considerably diminished if the wool is chromed before dyeing. The intense yellow color of exposed wool dyed by immersion in a cold aqueous solution of methyl orange is not removed by washing with water. Under similar conditions the color is readily removed from non-exposed wool.

The interior of exposed wool is alkaline, since it gives a bluish-violet color with haematin. The outer part is acid and gives a yellow-brown color. After prolonged exposure to sunlight, the wool becomes brittle and the fibers may be easily broken. Exposed wool is much more easily wetted than unexposed wool.

Irradiated wool fails to give the usual colors when treated with ninhydrin or allantoin because of the presence of sulfur dioxide.[73] The increase in the content of labile sulfur is also shown by the reduction of nitro- compounds to amines. Insolation also increases the primary amino-groups as determined by the van Slyke method.

[67] For further data obtained by the light of the carbon arc, see Appel, W. D., and Jessup, D. A., *Proc. Am. Assoc. Textile Chem. Colorists,* 350, 354, 1935; *J. Research Bureau Standards,* 15, 601 (1935).

[68] Kaneko, H., *Bull. Chem. Soc. Japan,* 9, 409 (1934); *Chem. Abs.,* 29, 662 (1935).

[69] Von Allwörden, K., *J. Soc. Chem. Ind.,* 35, 416 (1916); Naumann, K., *Ibid.,* 36, 707 (1917).

[70] Meunier, L., and Rey, G., *Rev. gen. mat. col.,* 28, 66 (1924); *J. Soc. Chem. Ind.,* 1924B, 370. *Compt. rend.,* 183, 596 (1926).

[71] Heermann, P., *Chem. Ztg.,* 48, 337 (1924).

[72] von Bergen, W., *Textilber.,* 6, 745 (1925); 7, 451 (1926); *Chem. Abs.,* 20, 2251 (1926); *Brit. Chem. Abs.,* B, 740 (1926).

[73] Meunier, L., and Rey, G., *Compt. rend.,* 183, 596 (1926); *Cuir Tech.,* 16, 530 (1927); *Chem. Abs.,* 22, 1047 (1928).

From 3.7 to 5.0 per cent of the sulfur content of cleaned wool samples is lost during exposure for 80 to 100 hours to the light from a quartz lamp.[74] This loss is more than doubled if the irradiation is followed by treatment with 0.001*N* sodium hydroxide. Microscopic examination shows the scales to be raised up; some are completely removed. It was suggested that the scales possess a higher sulfur content than the cortex so that a decrease in the number of scales explains in part the loss of the sulfur on irradiation.

Castiglioni [75] suggests that the yellowing of wool by ultraviolet light probably depends on the occurrence of the Salkowsky reaction between the sulfuric acid formed by oxidation of the sulfur of the wool and the cholesterol of the wool fat. Degreased wool tends to turn gray instead of the yellow to brown which forms in untreated wool.

The strength of wool is lost on exposure to light, slowly at first, then more rapidly and finally slowly again when but little strength is left.[76] Washing after exposure increases the loss of strength and results in a loss of weight owing to breakage of tendered surface hairs and to the dissolution of degradation products. Exposure also diminishes the extensibility. The product of extensibility and breaking load, a measure of the work of rupture, thus falls more rapidly than the breaking load itself and is probably a better measure of the useful strength of the cloth. The development of acidity is roughly parallel to the loss of strength. The Pauly test, however, gives positive results after a short exposure and soon reaches a maximum. Exposed cloth wets more rapidly and shrinks more when washed, but it fulls more slowly and has a lower regain.

Pretreatment of the wool with sulfuric acid is said to retard, and with alkalies to hasten, the deleterious action of light.[77] Rimington [78] has noted that free sulfhydryl groups are absent from normal wool and appear only after the action of alkalies or of ultraviolet light.

Smith and Harris [79] find irradiation of purified wool by the Fade-Ometer up to 100 hours progressively reduces its cystine content (from 12.2 to 7.9 per cent), with corresponding increases in ammonia nitrogen (0.28 to 1.22 mg. per gm.), alkali-solubility (11.9 to 36.2 per cent), and sulfate sulfur (0.06 to 0.37 per cent). Nearly all the sulfate sulfur in exposed wool is in the form of free sulfuric acid. There is a linear relation between cystine content and alkali-solubility in exposed wool. The deterioration is greater in wool previously treated by acid than in alkali-treated wool. The sulfur content of untreated and of acid-treated wool decreases during irradiation. This suggests that in the early stages, hydrogen sulfide is formed by a decomposition of the S—S group of cystine,[80] so that some is lost as hydrogen sulfide. The remainder is oxidized to sulfuric acid. Irradiation produces a type of oxidation different from that due to hydrogen peroxide. In nitrogen, hydrogen sulfide is evolved, the rate being increased by the presence of water.[81]

[74] Barritt, J., and King, A. T., *J. Textile Inst.,* 20, 151T (1929); *Brit. Chem. Abs.,* B, 846 (1929); see also Sommer, H., *Chem. Ztg.,* 51, 777 (1927).

[75] Castiglioni, A., *Chim. e l'Ind.,* 17, 82 (1935); *Brit. Chem. Abs.,* B, 540 (1935).

[76] Cunliffe, C. W., *J. Textile Inst.,* 27, T25 (1936); *Chem. Abs.,* 30, 3244 (1936).

[77] Sommer, H., *Chem. Ztg.,* 51, 777 (1927). See, however, Smith and Harris.[79]

[78] Rimington, C., *Biochem. J.,* 24, 205 (1930).

[79] Smith, A., and Harris, M., *Am. Dyestuff Reptr.,* 25, 383P, 542P (1936); *Brit. Chem. Abs.,* B, 828 (1936); *J. Research Bureau Standards,* 17, 97 (1936); *Rayon Textile Monthly,* 17, 501, 727, 795 (1936).

[80] See also McMahon, P. R., and Speakman, J. P., *Trans. Faraday Soc.,* 33, 844 (1937).

[81] Harris, M., and Smith, A. L., *J. Research Bureau of Standards,* 20, 563 (1938).

In order to ascertain the likelihood of oils staining textile fabrics, Gray [82] proposes to expose pieces of tape, treated with the oil, to the light of a quartz mercury arc, using a standard oil for purposes of comparison. A half-hour exposure at a distance of six inches from the lamp was found sufficient to develop a stain with oils likely to discolor fabrics.

Paine, Radley and Rendell obtain fabrics fluorescent in ultraviolet light by impregnating them with an aminostilbenesulfonic acid.[83, 84]

Photochemistry of Dyes [85]

Diazo-Compounds and Azo Dyes. According to Eggert and Schröter,[86] nitrogen is evolved at a constant rate during the photochemical decomposition of the diazo- compounds derived from 2-amino-α-naphthol-4-sulfonic acid and *p*-aminodiphenylamine. This diminishes gradually when the illumination is withdrawn. The quantum yield (about 0.35) is independent of the intensity and wave-length of the light and of the temperature and concentration of the diazo- solution. The same quantum yield is obtained when the solid compounds are studied. Schröter [87] also determined the rate of fading by comparison with color standards. The quantum yields so determined were somewhat higher, the deviations being considerable in the case of the product from *p*-aminodiphenylamine. The lower values found by measurement of the evolution of nitrogen are attributed to the occurrence of side reactions which inhibit the complete evolution of the liberated nitrogen. On adding acid, the yield is unchanged in the case of 2-amino-α-naphthol-4-sulfonic acid, but acid reduces that of the *p*-aminodiphenylamine compound from 0.52 to 0.35. Alkali reduced the quantum yield of the former to 0.15. With the latter, precipitation occurred. In alcohol solution, the yield is increased to 0.5 to 0.6 for both substances, possibly because of the formation of a soluble diazo-molecule-alcohol complex which favors the reaction.

Schmidt and Maier [88] concluded that the bleaching of 1,2,4-diazonaphtholsulfonic acid (long used in the preparation of light-sensitive papers) in acid solutions exposed to direct sunlight, proceeds quantitatively with evolution of nitrogen and replacement of the diazo- group by a phenol radical. The reaction was conducted in acid solution so that the disturbing formation of azo dye in the bleached solution could not take place. Fukushima and Horio [89] find the reaction due to rays shorter than 4500A, the photolysis being a reaction of zero order. It is not affected by change of temperature. The quantum yield was 0.16 at 3666A. The addition of salts [90] had no effect on the order of the reaction.

Horio [91] exposed papers treated with a series of diazo- compounds in a spectrograph to the mercury and tungsten arcs and found their spectral sensitivities to be simply related to their extinction coefficients, at least in the case of copying papers of 1-diazo-β-naphthol-4-sulfonic acid and of *p*-diazo-diphenylamine sulfate. In an extension of this work [92] in which various diazo- compounds on paper were similarly exposed to an iron arc, and developed with suitable azo- compounds, it was found that some benzenediazonium compounds were decomposed at wave-lengths less than 4000A, independently of the position of the substituent. The threshold values for light-sensitiveness coincide well with the limits of the molecular absorption.[93] Yamamoto [94] determined the effect of sunlight upon the rate of decomposition of α-naphthalene diazonium chloride. The velocity constant became twenty times greater in clear weather, 2.7 to 11 times greater when there was slight cloudiness, and was not increased in completely cloudy weather.

Crystal Scarlet is visibly oxidized and reduced when no special depolarizer is used in the presence of zinc oxide as photosensitizer.[95]

Ultraviolet light causes a gradual fading of 0.005 per cent Congo red, the reaction not being due to ozone.[96]

The photochemical reduction of methyl red in methanol by phenylhydrazine with chlorophyll solution as a photosensitizer by the wave-length 4358A is zero molecular in order, according to Ghosh and Sen-Gupta.[97] Its velocity is independent of the phenylhydrazine concentration and of temperature (25 to 35°C.) and reaches a maximum at a 5×10^{-5} molar concentration of chlorophyll. The quantum efficiency is 0.45 when only the radiation absorbed by the chlorophyll is considered. The dark reaction is extremely slow. In benzene, however, the reaction is unimolecular with a constant proportional to the phenylhydrazine concentration and a quantum yield of 0.05. For the wave-length 5460A, the reaction in both methanol and benzene is zero-molecular with a velocity independent of the phenylhydrazine concentration. The quantum yield varies between 1.0 and 0.1, decreasing with increasing chlorophyll concentration. If phenylhydrazine hydrochloride is used, the dark reaction has a measurable speed, independent of the chlorophyll concentration. The light reaction has a very low quantum yield and

[82] Gray, T. T., *Oil Paint and Drug Reporter*, Aug. 9, 1915.

[83] Paine, C., Radley, J. A., and Rendell, L. P., U. S. P. 2,089,413, Aug. 10, 1937; *Chem. Abs.*, **31**, 7264 (1937).

[84] For fluorescence tests applied to various textiles, see Derrett-Smith, D. A., *J. Textile Inst.*, **28**, T145 (1937); *Chem. Abs.*, **31**, 7256 (1937); Korda, P., and Déribéré, M., *Tech. moderne*, **29**, 355 (1937); Henk, H. J., *Kunsteide und Zellwolle*, **19**, 426 (1937); *Chem. Abs.*, **32**, 3620 (1938); Radley, J. A., *Analyst*, **63**, 266 (1938); *Chem. Abs.*, **32**, 4344 (1938); Tupholme, C. H. S., *Textile Colorist*, **60**, 441 (1938); Radley, J. A., *J. Soc. Dyers Colourists*, **53**, 376 (1937); Whittaker, C. M., *J. Soc. Dyers Colourists*, **53**, 468 (1937); *Chem. Abs.*, **32**, 1461 (1938). Undyed wool shows a weak violet fluorescence and undyed casein fiber a dead-white one. The results of ultraviolet-lamp readings should be considered as presumptive only, and should be rejected in the presence of contradictory evidence.

[85] For absorption data and a discussion of chromophore theories, see Brode, W. R., *Ber.*, **61B**, 1722 (1928); *Bureau Standards J. Research*, **2**, 501 (1929); *J. Am. Chem. Soc.*, **48**, 1984 (1926); **51**, 1204 (1929); Obreimov, I. V., and de Haas, W. J., *Proc. K. Akad. Wetensch. Amsterdam*, **32**, 1324 (1929); Blumberger, J. S. P., *Chem. Weekblad*, **25**, 282, 315 (1928); **29**, 454 (1932); **30**, 538 (1933); **32**, 6, (1935); Hodgson, H. H., and Rosenberg, W., *J. Soc. Chem. Ind.*, **49**, 405T (1930); Szegö, L., *Ber.*, **61B**, 2087 (1928); **62B**, 736 (1929); Cambi, L., and Szegö, L., *Ber.*, **61B**, 2081 (1928); Funkhouser, J., and Brode, W., *J. Am. Chem. Soc.*, **56**, 2172 (1934); Piper, J., and Brode, W., *J. Am. Chem. Soc.*, **57**, 135 (1935); Chakravarti, G. C., *J. Indian Chem. Soc.*, **8**, 503 (1931); Mangini, A., *Gazz. chim. ital.*, **65**, 298, 308 (1935); Barkoff, S., *Bull. soc. chim.*, **2**, 1288 (1935); Foster, D. G., *J. Am. Chem. Soc.*, **53**, 654 (1931); Maki, T., *J. Soc. Chem. Ind. Japan*, **34**, 496 (1931); Luszcak, A., and Grün, L., *Monatsh.*, **64**, 349 (1934); Griffith, M. E., and Brode, W. R., *Ohio Agr. Expt. Sta., Bimonthly Bull.*, **192**, 122 (1938); *Chem. Abs.*, **32**, 7732 (1938); Lazarev, P., *Chimie et Industrie*, Special No., 457 (1928); Schumm, O., "Die spektrochemische Analyse natürlicher organischen Farbstoffe," Jena, Fischer; Zintl, E., and Rauch, A., *Ber.*, **58B**, 234 (1925); Hirschler, L., *Biochem. Z.*, **190**, 411 (1927); Szilard, A., *Ibid.*, **170**, 185 (1926); Speas, W., *Phys. Rev.*, **31**, 569 (1928); Merritt, E., *Ibid.*, **28**, 684 (1926); Prideaux, E., *J. Soc. Chem. Ind.*, **45**, 664, 678, 697 (1926); Dutt, S., *Quart. J. Indian Chem. Soc.*, **4**, 99 (1927); Holmes, W., and Peterson, A., *J. Phys. Chem.*, **36**, 633 (1932); Hewitt, J., *Sci. J. Roy. Coll. Sci.*, **3**, 27 (1933); Scheibe, G., *Kolloid-Z.*, **82**, 1 (1938); Scheibe, G., and Kandler, L., *Naturwiss.*, **26**, 412 (1938); Sen-Gupta, S. B., *J. Indian Chem. Soc.*, **15**, 263 (1938); *Chem. Abs.*, **32**, 8939 (1938).

[86] Eggert, J., and Schröter, W., *Z. Elektrochem.*, **34**, 602 (1928).

[87] Schröter, W., *Z. wiss. Phot.*, **28**, 1 (1930); *Chem. Abs.*, **25**, 43 (1931).

[88] Schmidt, J., and Maier, W., *Ber.*, **64B**, 767, 778 (1931).

[89] Fukushima, I., and Horio, M., *J. Soc. Chem. Ind. Japan*, **34**, 372, 374 (1931); *Chem. Abs.*, **26**, 2377 (1932); *Mem. Coll. Eng. Kyoto Imp. Univ.*, **6**, 179 (1931); *Chem. Abs.*, **25**, 4797 (1931).

[90] Kogan, N. M., Pischulina, A. F., and Ankinovich, A. G., *Anilinokrasochnaya Prom.*, **2**, No. 11, 34 (1932); *Chem. Abs.*, **27**, 5321 (1933).

[91] Horio, M., *Mem. Coll. Eng. Kyoto Imp. Univ.*, **8**, No. 1, 26 (1934); *Chem. Abs.*, **28**, 5338 (1934).

[92] Horio, M., *J. Soc. Chem. Ind. Japan*, **37**, 322 (1934); *Chem. Abs.*, **28**, 6637 (1934).

[93] The results have also been extended to solutions containing, in addition to the diazo- compound, varying amounts of Crystal Scarlet 6RA Extra and of Orange II. Horio, M., and Yamashita, S., *Z. wiss. Phot.*, **33**, 273 (1935); *Brit. Chem. Abs.*, **A**, 713 (1935).

[94] Yamamoto, E., *J. Soc. Chem. Ind. Japan*, **38**, 275B (1935); *Chem. Abs.*, **29**, 6492 (1935).

[95] Fukushima, I., Horio, M., and Ohmori, M., *J. Soc. Chem. Ind. Japan.*, **35**, 398B (1932); *Chem. Abs.*, **26**, 5848 (1932).

[96] Puchkovskii, B. S., and Nekludov, V. N., *Kolloid-Z.*, **66**, 191 (1934); *Chem. Abs.*, **28**, 2623 (1934).

[97] Ghosh, J. C., and Sen-Gupta, S. B., *J. Indian Chem. Soc.*, **11**, 65 (1934); *Chem. Abs.*, **28**, 3662 (1934).

small temperature coefficient. Its unimolecular constant is proportional to the concentration of the reducing salt. An activated complex of chlorophyll and methyl red is believed to play a part in the reaction mechanism.

Since the photolytic oxidation of cellulose is accompanied by the evolution of carbon dioxide and since cotton dyed with simple azo-dyes yields more carbon dioxide upon irradiation than undyed cotton, Haller and Ziersch [98] conclude the dye fading to be an oxidative process. The carbon dioxide production is greater when the samples are exposed in an atmosphere rich in oxygen.

Exposure of a dilute (1:10,000) aqueous solution of 1-*p*-sulfobenzeneazo-N-phenyl-β-naphthylamine to sunlight gives *ang.* naphtho-phenazine and mainly the betaine of 3-phenyl-2-*p*-sulfophenyl-$\alpha\beta$-naphth-1,2,3-triazolium hydroxide.[99] Exposure of 1-benzeneazo-N-phenyl-β-naphthylamine on cotton immersed in water gives after concentration of the extract and treatment with picric acid, 2,3,-diphenyl-$\alpha\beta$-naphth-1,2,3-triazolium picrate, but not *ang.* naphtho-phenazine. The N-benzyl derivative of 1-benzeneazo-N-phenyl-β-naphthylamine is much more stable to light. Diphenyl-4,4-*bis*-(8-azo-N-phenyl-β-naphthylamine) on cotton is bleached rapidly by sunlight in air or oxygen. In nitrogen, bleaching is very slow. Azo- dyes from N-alkyl-β-naphthylamines are not so readily convertible into triazolium salts and are much more stable in light.

Golden yellow solutions of $(C_6H_5)_3CN{=}NC_6H_5$ are decolorized rapidly when exposed to light of short wave-lengths.[100]

Triphenylmethyl and Triphenylmethane Dyes. The free radical, triphenylmethyl, was found by Gomberg and Cone [101] to be bleached in sunlight in benzene solution with the production of triphenylmethane and unidentified substances. Schmidlin and Garcia-Banús [102] and, more recently, Bowden and Jones [103] found the products to be triphenylmethane and diphenyl-*bis*-diphenylenethane. The process occurs slowly in diffused light. Visible light (5300-4000A) is the most active portion of the spectrum. The presence of triphenyl peroxide or triphenylchloromethane does not alter the reaction, but the nature of the solvent has a marked effect on the rate of the reaction. In toluene, decolorization was more rapid than in benzene; in 1,3,5-trimethylbenzene and *m*-xylene it was even faster, and in hexane, the most rapid. No loss of color was observed in sulfur dioxide solutions and in the solid state the photochemical change was of a low order.

Triphenylmethyl peroxide has been obtained in 45 per cent yield by exposing a cyclohexane solution of triphenylbromomethane with air or oxygen for eight days to light (less than 3800A) from a Pyrex mercury arc.[104] It is highly probable that triphenylmethyl and bromine are formed by primary dissociation.

According to Tănăsescu,[105] 2,4-dinitrotriphenylmethane on insolation in neutral solutions yields the red O-quinone derivative, and in pyridine, the green nitrosocarbinol. In sunlight, 5-chloro-2-nitro-4′,4″-diaminotriphenylmethane gives [106] a blue compound and a compound $C_{38}H_{30}O_2N_6Cl_2$, reduced by tin and hydrochloric acid to 2,4,′4″-triaminotriphenylmethane. Similarly, 2-nitro-4′,4″-diaminotriphenylmethane gives a blue compound and a compound $C_{38}H_{32}O_2N_6$. The diethylmercaptol of Michler's ketone [107] quickly turns green in light, especially when moist. A solution of triphenylmethane and triphenylchloromethane in light forms triphenylmethyl reversibly.[108]

[98] Haller, R., and Ziersch, G., *Melliand Textilber.*, **10**, 951 (1929); *Chem. Abs.*, **24**, 3373 (1930).
[99] Krollpfeiffer, F., Mühlhausen, C., and Wolf, G., *Annalen*, **508**, 39 (1933); see also Witt, O. N., *Ber.*, **20**, 571 (1887).
[100] Lifschitz, I., *Ber.*, **58B**, 2434 (1925).
[101] Gomberg, M., and Cone, L. H., *Ber.*, **37**, 3545 (1904).
[102] Schmidlin, J., and Garcia-Banús, A., *Ber.*, **45**, 1344 (1912).
[103] Bowden, S. T., and Jones, W. J., *J. Chem. Soc.*, 1149 (1928).
[104] Halford, J. O., and Anderson, L. C., *Proc. Nat. Acad. Sci.*, **19**, 759 (1933).
[105] Tănăsescu, I., *Bull. soc. chim.*, **39**, 1718 (1926); see also *Chem. Abs.*, **21**, 533 (1927) for *o*-nitrotriphenylmethane.
[106] Tănăsescu, I., and Suciu, M., *Bull. soc. chim.*, **4**, 245 (1937); *Brit. Chem. Abs.*, A II, 375 (1937).
[107] Madelung, W., *J. prakt. Chem.*, **114**, 1 (1926).
[108] Schlenk, W., and Herzenstein, A., *Ber.*, **43**, 3545 (1910).

$$(C_6H_5)_3C.Cl + (C_6H_5)_3CH \longrightarrow HCl + 2(C_6H_5)_3C$$

It has long been known [109] that the leucobases of triphenylmethane dyes (brilliant green, malachite green, crystal violet, etc.) are highly light-sensitive, readily producing the corresponding dyes. König [110] made some attempts to utilize these photooöxidations in color photography. Eder [111] believed that, mixed with collodion, the leucobases form films more light-sensitive than the dyed silver halide films previously used in the photometry of the visible region. Carroll [112] found these reactions to show no induction periods and to be proportional to the light intensity. The sensitivity was, however, too low for practical photographic application, although the oxidations may be accelerated by nitrogen bases, as heterocyclic and aliphatic amines.

Little use has been made of this behavior in actinometry. An important application of crystal violet and, particularly, malachite green in actinometry is, however, based upon a reaction of their leucocyanides, originally described by Lifschitz.[113] It had been known that the addition of potassium cyanide to a triphenylmethane dye bleaches it with the production of a colorless triarylacetonitrile. Lifschitz showed that the colorless alcoholic solutions of the latter products were rapidly converted into the corresponding dyes when irradiated by an iron-nickel arc. The change occurred but slowly in sunlight in glass, so that it is due to the ultraviolet rays. When placed in darkness, the dyes again lose their colors. The leucocyanides in alcohol were not electrolytes. Irradiation was believed to convert them into colored, dissociated dye ions and cyanide ions, since the conductivity could be shown to increase. It was possible to demonstrate the liberation of the cyanide ion by setting up concentration cells of dark and illuminated solutions with silver cyanide coated electrodes.

Similar behavior was encountered in the thiocyanates and sulfonates of the triphenylmethane dyes, as well as in the dihydroxy-derivatives (benzaurin) and in unsubstituted triphenylmethyl cyanide. It became apparent that triphenylmethane derivatives can exist both in non-electrolyte and electrolyte forms. The primary photochemical effect was believed to consist in the transfer of a valence electron from the carbon atom to the cyanide or other group, which thereby becomes an ion. The triphenylmethyl ion need not, however, be colored until after it has undergone a further constitutional alteration. Lifschitz represented the process as follows:

$$\underset{\substack{\text{Colorless,}\\ \text{undissociated}}}{(R_2NC_6H_4)_3CCN} \underset{\text{Dark}}{\overset{\text{Light}}{\rightleftharpoons}} [(R_2NC_6H_4)_3C]^+ + CN^- \underset{\text{Dark}}{\rightleftharpoons} \left[C(C_6H_4NR_2)_2{=}C_6H_4{=}NR_2 \right]^+ + CN^-$$

Harris, Kaminsky and Simard,[114] who studied the absorption spectra of the leucocyanides and products of photolysis of malachite green, found the Lifschitz mechanism inadequate to account for the phenomenon of fading of the color. They found the addition of water to the alcoholic (95-per cent) solutions to increase the rate of fading, which could be similarly accelerated by potassium hydroxide or

[109] Gros, O., *Z. physik. Chem.*, **37**, 157 (1901).
[110] König, E., *Z. Angew. Chem.*, **17**, 1633 (1904).
[111] Eder, J. M., *Phot. Korr.*, **56**, 140 (1919); *Chem. Zentr.*, **90**, 396 (1919); *J. Soc. Chem. Ind.*, **38**, 878 (1919).
[112] Carroll, B. H., *J. Phys. Chem.*, **30**, 130 (1926).
[113] Lifschitz, I., *Ber.*, **52**, 1919 (1919); **58B**, 2434 (1925); Lifschitz, I., and Joffe, C., *Z. physik. Chem.*, **97**, 426 (1921).
[114] Harris, L., Kaminsky, J., and Simard, R., *J. Am. Chem. Soc.*, **57**, 1151 (1935).

cyanide. No dark reaction could be observed if hydrochloric acid was added either before or after the photochemical production of the color. The addition of the acid to partly faded solutions restored the color completely, unless the water content of the solutions exceeded 20 per cent, in which case there was only a 95 to 97 per cent restoration of the color. No color appeared when hydrochloric acid was added to a non-irradiated leuco-cyanide solution. This indicated that the product of the dark reaction in 95-per cent alcohol is not the original leucocyanide. In their modified mechanism, importance was attached to hydrolysis of the photocompound. In the absence of hydrochloric acid, the final product of the dark reaction was assumed to be the colorless carbinol and not the original leucocyanide. Accordingly, they proposed the following scheme:

$$\underset{\text{Colorless, non-dissociated}}{[(CH_3)_2NC_6H_4]_2C_6H_5{\equiv}C{-}CN} \xrightarrow[\text{Ia}]{\text{Light}} \underset{\text{Colored}}{[(CH_3)_2NC_6H_4]_2C_6H_5 \equiv CCN}$$

$$\text{II} \downarrow \qquad\qquad \downarrow$$

$$\underset{\text{Colorless, non-dissociated}}{[(CH_3)_2NC_6H_4]_2C_6H_5{\equiv}COH} \xrightarrow[\text{IV}]{\text{HCl}} \underset{\text{Colored.}}{\{[(CH_3)_2NC_6H_4]_2C_6H_5{\equiv}C\}^+Cl^-}$$

The carbinol can undergo a photolysis to the colored compound, which accounts for the regeneration by light of the partly decolorized solution. It was assumed that reaction I is instantaneous, but that reaction III may be slow or moderate. Reaction IV was known to be comparatively slow from measurements made with the pure carbinol. Reactions II and IV were found to be fast if hydrochloric acid was used during the photolysis. No evidence could be found for the formation of an intermediate compound in Ia. The dark reaction had a positive temperature coefficient. Ariga [115] observed also that the colorless solution of malachite green produced by the action of alkali rather than cyanide (probably a colorless pseudo-ammonium base) regains its color when irradiated by a mercury arc or intense sunlight. The unimolecular rate constant was independent of the alkali concentration and temperature, but was proportional to the light intensity.

The Lifschitz reaction was made the basis of a useful actinometric solution by Weyde and Frankenburger,[116] who used a pure alcoholic solution of the leuco-cyanide of crystal violet. The quantum yield of the color formation is unity for the wave-lengths 2537 and 3130A. If enough cyanide was added to insure reversal in darkness, the solution was found to be suitable for use by physicians and meteorologists for measuring the erythema-producing rays of sunlight or artificial sources. In the case of this dye, the reverse dark reaction has a temperature coefficient of five. Its rate is proportional to the dye concentration and is greatly diminished by the presence of a little water.

For a precision actinometer, Harris and Kaminsky [117] found the malachite green leucocyanide to be superior, since it has thirty times the solubility of the crystal violet leucocyanide. It was especially suited for the region between 3340 and 2480A. With malachite green, a shorter cell-length may be used with certainty of 99.9-per cent absorption, the correction for inner-filter action by the photocompound is less, and colorimetric measurements can be made more accurately for the green dye. The quantum yield is unity.

Relatively little is known of the bleaching of the triphenylmethane dyes.

[115] Ariga, T., *Bull. Chem. Soc. Japan*, **2**, 65 (1927); *Chem. Abs.*, **21**, 2103 (1927).
[116] Weyde, E., and Frankenburger, W., *Trans. Faraday Soc.*, **27**, 561 (1931); Weyde, E., Frankenburger, W., and Zimmermann, W., *Z. physik. Chem.*, **17B**, 276 (1932).
[117] Harris, L., and Kaminsky, J., *J. Am. Chem. Soc.*, **57**, 1154 (1935).

Henriquez [118] believed that exposure of aqueous crystal violet solutions for several days converts it into a red dye, assumed to be fuchsine, by a replacement of the methyl groups by hydrogen. The presence of a free amino-group could be proved by diazotation and coupling reactions. Under similar conditions, malachite green was believed to be converted into Doebner's violet. With visible light, these color changes were more rapid than the bleaching of the dyes, but ultraviolet light destroys the colors, the more rapidly the more basic the solution. The oxidation of fuchsine by hydrogen peroxide is also brought about by ultraviolet light, the amino-groups being unaffected. Iwamoto [119] states that in the presence of air and light, malachite green oxalate and crystal violet oxalate are converted into *p*-dimethylaminoacetophenone and Michler's ketone, respectively. In a sealed tube, the crystal violet oxalate gives the leuco- compound. Weyde, Frankenburger and Zimmermann [120] found that on prolonged irradiation of alcoholic solution containing potassium cyanide, the leucocyanide is completely destroyed, probably by oxidation.

Phthalein Dyes. The radiation of an arc light has been said to increase the rapidity of the oxidation of phenolphthalin to phenolphthalein.[121]

Fluorescein in glycerol solution exhibits a blue rather than a green fluorescence when irradiated by ultraviolet light. This is gradually and permanently lost on prolonged irradiation by wave-lengths shorter than 2540A. Glycerol solutions of methylene violet, corallin, crocein, esculin, erythrosin, eosin and rhodamine similarly lose their fluorescent properties on exposure to ultraviolet light. Solutions of erythrosine, eosin and rhodamine in benzyl alcohol are much more sensitive to the action of light than are the glycerol solutions.[122]

It has been suggested [123] that the bleaching of fluorescein dyes by light is a process of oxidation by hydrogen peroxide probably formed from water and oxygen, this reaction requiring an activation of the dye molecule by light.

Reychler [124] found no iodine liberated in darkness from solutions containing 0.125 gm. potassium iodide, 0.5 gm. of potassium dichromate and 0.01 gm. of eosin per 100 cc. in three hours. In weak diffused light after forty minutes the iodine liberated was equivalent to 2.8 cc. of 1-per cent sodium thiosulfate solution. After two and ten minutes in sunlight, the amounts of thiosulfate used were 6.3 and 16.4 cc.

In the presence of reducing agents, eosin is not hydrogenated [125] in darkness, even in warming. In sunlight or the light of a quartz lamp, it is almost instantly hydrogenated. The color returns quickly in darkness unless the irradiation has been unnecessarily prolonged, in which case the eosin is irreversibly changed into a strongly fluorescing substance.

Methylene Blue. Nurnberger and Arnow [126] find that aqueous solutions of methylene blue have two regions of absorption with maxima at 2920 and 2460A. Irradiation of the solution with a mercury arc causes a decrease in the absorption in the visible and ultraviolet, the effect being greatest in the solutions of highest pH. The wave-lengths most active in decreasing the absorption are shorter

[118] Henriquez, P. C., *Rec. trav. chim.*, **52**, 991 (1933).
[119] Iwamoto, K., *Bull. Chem. Soc. Japan*, **10**, 420 (1935); *Brit. Chem. Abs.*, **B**, 1090 (1935).
[120] Weyde, E., Frankenburger, W., and Zimmermann, W., *Z. physik. Chem.*, **17B**, 276 (1932).
[121] Rossi, G., *Chem. Zentr.*, **82**, 1659 (1911); *Giorn. Farm. Chem.*, **60**, 433 (1911).
[122] Asterblum, M., *Bull. Intern. Acad. Polonaise*, **A7-8**, 297 (1924); *Chem. Abs.*, **20**, 1562 (1926).
[123] Blum, H. F., and Spealman, C. R., *J. Phys. Chem.*, **37**, 1123 (1933); see also Chakravarti, D. N., and Dhar, N. R., *Z. anorg. Chem.*, **142**, 299 (1925).
[124] Reychler, A., *Bull. soc. chim. Belg.*, **34**, 236 (1925); *Chem. Abs.*, **20**, 544 (1926).
[125] Kögel, G., and Steigmann, A., *Phot. Ind.*, 1169 (**1925**); *Chem. Abs.*, **20**, 1035 (1926).
[126] Nurnberger, C., and Arnow, L., *J. Phys. Chem.*, **38**, 71 (1934).

than 2700A. For this reason, the change in absorption by aqueous solutions of methylene blue cannot be used as a measure of the light intensity in the physiologically active region between 2900 and 3100A.

Most photochemical studies on this dye have been concerned with coupled or sensitized processes. Brandt [127] studied the iron-sensitized reduction in the presence of ethanol and a phosphate buffer at pH 8.6. A considerable dark reaction occurred only when both alcohol and ferrous ions were present, and it was in such solutions that the greatest photosensitization was observed. The reduced solutions were reoxidized in the dark, an equilibrium being established which is displaced toward the side of leuco-methylene blue.

In light, zinc oxide acts on aqueous solutions of organic dyes of widely different classes.[128] In pure, air-free aqueous solution, the dyes are both oxidized and reduced. In the presence of an anodic depolarizer, they are exclusively reduced. With vat dyes, photolysis still occurs even at the highest reduction potentials, 0.15 v. in the case of safranine. A considerable difference in potential between the anodic and cathodic processes can be overcome by light. With azo-dyes, the photolytic reduction is not reversible, the products not reforming dyes on exposure to the air. Under certain conditions, sensitizing dyes can act upon other dyes as does zinc oxide. The necessary condition is that the absorption region of the sensitizing dye must coincide with that of the acceptor on the short wave-length side.

In the presence of zinc oxide as photosensitizer, Arro [129] found no vat dye formed during the bleaching of methylene blue. But in the presence of an anodic depolarizer (dextrose), the velocity of fading is increased and some vat dye is formed. The sensitizing action of yellow mercuric oxide is greater, and that of cadmium oxide, yellow lead oxide and the uranyl ion, less than that of zinc oxide. The addition of manganese dioxide, uranium dioxide or cadmium oxide increases the action of zinc oxide. The bleaching is irreversible.

Pyruvic acid, "Kojic" acid, ethyl acetoacetate, phloroglucinol and resorcinol reduce the dye in the absence of oxygen when irradiated.[130]

The enzymatic reduction of the dye by *Bacterium pasteurianum* and by liver extracts is also speeded up by light. The dye molecule and not the hydrogen donor or the dehydrase is activated in the photochemical reaction.

The equilibrium potential of the methylene blue and phenylhydrazine sulfonate reaction is light-sensitive,[131] the direction of the displacement of the equilibrium being opposite in light from the two ends of the visible spectrum. Hellström [132] has observed that the redox potential of the methylene blue-ferrous ion system decreases reversibly in light, the potential change being dependent on the pH. However, the potential of the iron-free 50-per cent reduced dye is not affected by light, and the addition of ferrocyanide does not make it photosensitive. Light activation of the dye may cause the formation of a methylene blue-iron complex.

A procedure advocated by Marie and Raleigh [133] for the treatment of methylene blue for use in biological stains consists in dissolving one gram in 100 cc. of aqueous 0.5-per

[127] Brandt, K. M., *Arkiv Kemi, Mineral Geol.*, **12B**, No. 7 (1935); *Chem. Abs.*, **30**, 386 (1936); see also Weiss, J., *Trans. Faraday Soc.*, **32**, 1331 (1936).

[128] Neuweiler, C., *Z. wiss. Phot.*, **25**, 187 (1928); *Brit. Chem. Abs.*, **1928A**, 457.

[129] Arro, H., *Commentationes Univ. Tartu* **A18**, (5) 3 (1930); *Chem. Abs.*, **26**, 4255 (1932).

[130] Tamiya, H., Hida, T., and Tanaka, K., *Acta Phytochim.*, **5**, 119 (1930); *Chem. Abs.*, **25**, 1531 (1931).

[131] Holst, G., *Z. physik. Chem.*, **A175**, 99 (1935); **179A**, 172 (1937); *Nature*, **139**, 285 (1937).

[132] Hellström, H., *Naturwiss.*, **24**, 76, 217 (1936).

[133] Marie, S. V., and Raleigh, J. T., *J. Lab. Clin. Med.*, **10**, 250 (1924).

cent sodium bicarbonate solution and exposing in an open shallow dish to an arc lamp for ten to thirty minutes. When cool, there is slowly added 500 cc. of 0.1-per cent yellowish eosin solution until the surface becomes purplish with a metallic luster and a fine black powder is formed on the surface. After filtering and air-drying 0.1 gram is dissolved in 60 cc. of acetone free from methanol.

Irradiation of methylene blue, thionine, or brilliant cresyl blue in acid ferrous sulfate with the visible light of a strong carbon arc produces bleaching or a change in color, due to the formation of leuco- dyes, which is irreversible if the ferric ion formed is precipitated by hydrolysis. In darkness, the process is completely reversible, the ferric ion being reduced by the leuco- dye.[134] In the absence of the dye the irradiation of a 0.5 molar solution of ferrous sulfate in sulfuric acid by a strong mercury arc produces hydrogen when oxygen is excluded.

The rate at which Lauth's violet is bleached in aqueous methanol solution in the presence of diethyl-β-allylthiocarbamide as acceptor rises rapidly toward a limiting value as the concentration of the latter is increased, and at the same time the temperature coefficient falls. Hydroquinone, pyrogallol, and phenol retard the bleaching and also reduce the fluorescence of sodium naphthionate, the relative efficiencies being similar in each case. The part played by these substances in both processes depends on the deactivation of activated molecules by collisions. At high concentrations, electrolytes either accelerate the bleaching somewhat or retard it but slightly, although with small concentrations of some salts, there is a pronounced retardation.[135]

If a 0.001-per cent aqueous solution of Lauth's violet (thionine) containing a small amount of ferrous sulfate (0.0075 mole per liter) and 0.01 molar sulfuric acid is cooled to $-10°$C. and exposed to the light of a powerful arc light, the dye is bleached in one or two seconds by a reversible process. The higher the temperature and the weaker the light, the slower the reduction. Lauth's violet has a positive reduction potential, 0.045 v. Methylene blue, Nile blue, phenosafranine and neutral red, all of which have negative normal reduction potentials, do not behave in a similar manner. In the case of methylene blue, photoreduction occurs if the ferrous sulfate is replaced by potassium ferrocyanide, which has a more negative reduction potential. The phenomenon can be explained by supposing that the photoexcited molecule (Lauth's violet) has a more positive reduction potential than the unexcited molecule, and even more positive than that of the ferric-ferrous ion system. Therefore, a reaction can occur with the formation of leuco- base and ferric ion. The maximum of the absorption band of Lauth's violet at 6000A corresponds to an energy (47,370 cals. per mole) more than sufficient for the above change. Methylene blue has a more negative reduction potential than Lauth's violet and its absorption maximum lies at longer wave-lengths (6700A) so that the energy absorbed is insufficient for the reaction to occur.

Bleaching of Dyes. The rate of loss of color of indigocarmine in ammonium oxalate solution by atmospheric oxidation under the influence of violet light obeys the law of mass action for concentrations ranging between 1 per cent and one to twenty thousand.[136] Similarly, the oxidation of helianthine follows the law, even in the range of concentrations in which solutions exhibiting an appreciable fluorescence do not follow it.

[134] Weiss, J., *Nature*, **136**, 794 (1935). See, however, Weber,[137] Leuco methylene blue turns blue in the light and is decolorized by standing in the dark, according to Matiu, A. I., and Popescu, C., *Bull. soc. chim.*, **4**, 1230 (1937). This had been previously observed by W. M. Clark, *U. S. Public Health Reports*, **40**, No. 23, 1131-1201 (1925).

[135] Weber, K., *Z. physik. Chem.*, **15B**, 18 (1931); *Naturwiss.*, **23**, 849 (1935).

[136] Perrin, J., and Choucroun, N., *Compt. rend.*, **187**, 697 (1928).

An increase of temperature between 15 and 45°C. retards the photochemical decolorization of benzene solutions of cyanine and gallocyanine.[137]

Aside from the detailed studies which have been made on the photochemistry of individual dyestuffs, there have been many observations of the bleaching of dyestuffs in general. Some have contributed essential data on the relative light-fastness of different classes of dyestuffs. Others have been more or less speculative but have in some instances at least brought forward stimulating suggestions as to the mechanisms concerned.[138]

Steigmann[139] raises the question as to why certain dyes are light-fast despite the absorption of energy by their chromophores. He suggests that in certain cases there may be a preferential action on other light-sensitive groups present in the molecule which cause an "intra-molecular desensitization." For this he considers alizarin an example. In other dyes, certain other groups, or configurations may exert an inhibitory action, but in this case the nature of the transformations of the absorbed energy is obscure.

Although some workers have found light to convert certain dyes, particularly of the triphenylmethane series, into other dyes, Barat and Dutt[140] find that, in general, sunlight decomposes dyestuffs directly into colorless products. In other words, the net effect is practically the same as that of a gradual dilution of the dye solution until its color becomes invisible. Spectrophotometric studies of the bleaching of a number of dyes have been published by Alberts.[141]

Leiber[142] studied the effect of daylight in altering the absorption spectra of films of dyed gelatin made by pouring 10 cc. of an 8-per cent solution of the dye over a 100 sq. cm. glass mold. The dyes fell into three classes: (1) Bleaching makes the dye density gradually decrease. (2) A region of strong absorption was decreased and a field of weak absorption was strengthened. (3) The absorption maximum was displaced to other wave-lengths. The latter two classes were not entirely distinct. The following dyes were not affected by exposure to sunlight for 28 days and are suitable for the preparation of photographic filters: Crystal Ponceau 6R, Orange II, Pyrazole Yellow, Rapid Filter Yellow, Naphthol Green, Toluidine Green and Toluidine Blue.

The change of conductance of collodion films colored by cyanine, pinaverdol and pinachrome was observed by an electrometric method by Zchodro[143] during illumination. The collodion itself is unaffected by white light. The conductivity of the film increases with the time of illumination and at first is proportional to the time, but on longer exposures, the increase becomes less rapid and the conductivity gradually reaches a constant value. After the illumination ceases, the conductivity gradually diminishes. Cyanine showed a maximum conductivity at around 6000A, pinaverdol at about 5700A and pinachrome a sharp maximum at about 5800A. Irradiation of a solution of cyanine in benzene produced a decrease in its electrical resistance, which rose again when the illumination ceased. Illumination with monochromatic light had this effect only when its wave-length was in the absorption band of the solution. Kosche[144] finds Indigosol IBL darkens in light, probably because of oxidation. Not all indigosol dyes are light-sensitive.

[137] Zchodro, N., *J. chim. phys.*, **26**, 178 (1929); *Chem. Abs.*, **23**, 3166 (1929).
[138] Kögel, G., *Phot. Korr*, **68**, 83 (1932); *Chem. Abs.*, **26**, 5507 (1932).
[139] Steigmann, A., *Z. wiss. Phot.*, **27**, 268 (1929); *Brit. Chem. Abs.*, **A**, 174 (1930).
[140] Barat, K., and Dutt, S., *Quart. J. Indian Chem. Soc.*, **4**, 265 (1927); *Chem. Abs.*, **21**, 3194 (1927).
[141] Alberts, H., *Z. wiss. Phot.*, **33**, 234, 249 (1935).
[142] Leiber, F., *Kolloid-Z.*, **50**, 68, 117 (1930).
[143] Zchodro, N., *J. chim. phys.*, **26**, 59, 117 (1929); *Chem. Abs.*, **24**, 1578 (1930).
[144] Kosche, S., *Klepzig's Textil-Z.*, **40**, 584 (1937); *Chem. Abs.*, **32**, 6465 (1938).

Crespi[145] found no parallelism between the action of solar and ultraviolet radiation in their effects on cotton dyes. Ozone formation played no part in the action of the latter radiation. Evidence in support of an oxidation mechanism has been advanced by several workers. Scharwin and Pakschwer[146] exposed methylene blue, crystal violet, Congo red and eosin on cotton or paper in glass tubes in which were sealed various gases, to the action of sunlight or the light of a mercury arc. The speed of bleaching decreased in various gases in the following order: oxygen, nitric oxide, nitrous oxide, carbon monoxide, carbon dioxide, hydrogen, nitrogen. No bleaching was observed under nitrogen and generally none with hydrogen, although in the latter case, decided changes due to reduction sometimes occurred. In oxygen, nitric oxide and nitrous oxide, carbon dioxide could always be detected after the exposure to sunlight. The changes due to oxidation were irreversible. When the dye was absorbed in porous clay, the amount of carbon dioxide produced after four months in sunlight was much less than in cases in which cotton was the substrate.

It has recently been pointed out that in practice consideration must be given not so much to the effect of light on a dye as to its effect on the entire fiber-dye system. A single dye may also fade, but may be permanent when present in admixture with a more resistant dye.

An early theory of the bleaching mechanism due to Gebhardt[147] assumed the intermediate formation of an organic peroxide of the dye, but not of hydrogen peroxide. The earlier literature of the fading of dyes on cotton fabrics was reviewed by Cunliffe.[148]

Plain calico and similar fabrics dyed with Brilliant Copper Blue, Chlorazol Sky Blue and Benzopurpurin 4B were found by Miss Hibbert[149] to have almost unchanged copper numbers after exposure to 669 hours of bright sunshine. Since complete destruction of the dyes occurred long before the copper number of the fabric reached 3.6, it was concluded that the fading of dyed cotton is not due to a reducing action of the cellulose under the influence of light, as had been previously assumed.[150] Certain dyes retard or accelerate the tendering of cotton. Cotton fabrics dyed with Duranthrene Yellow, Cibanone Yellow and Indigo, which had an original tensile strength of 48 lbs. had tensile strengths of 27, 16 and 22 lbs., respectively, after exposure for 120 hours in a Fade-Ometer. Isatin could be obtained in a pure state by extraction from calico which had been dyed with indigo and exposed to light.[151] In cotton materials dyed with chrome green, chromium hydroxide had a marked protective effect against sunlight.

According to Seyewetz and Mounier,[152] nitrated coloring matters turn brown under the action of light, which probably has a reducing action. The brown substance is insoluble in water and slightly soluble in alcohol, but too little could be isolated for its composition to be determined.

Cotton fabrics dyed with *o*-tolueneazo-β-naphthol became covered with bright lustrous crystals after exposure for three minutes to the light from a Fade-

[145] Crespi, E., *Atti congresso naz. chim. pura applicata*, **2**, 833 (1926); *Chem. Abs.*, **22**, 3532 (1928).
[146] Scharwin, W., and Pakschwer, A., *Z. angew.* Chem., **40**, 1008 (1927).
[147] Gebhardt, K., *Z. angew. Chem.*, **22**, 2484 (1910); **23**, 820 (1910); *J. Chem. Soc.*, **98**, 405 (1910).
[148] Cunliffe, P. W., *J. Textile Inst.*, **15**, 173; see also Ellis, G. H., *Chem. Age.*, **13**, 470 (1925); Barker, S., and Hirst, H., *J. Textile Inst.*, **17**, 483T (1926).
[149] Hibbert, E., *J. Soc. Dyers Colourists*, **43**, 292 (1927); *Chem. Abs.*, **43**, 292 (1927); *Brit. Chem. Abs.*, **B**, 840 (1927).
[150] See Harrison, W., *Ber.*, **47**, 689 (1914).
[151] See also Haller, R., Hackl, J., and Frankfurt, M., *Textilber.*, **9**, 415 (1928); *Brit. Chem. Abs.*, **B**, 479 (1928). In contrast to Indanthrene Yellow, the fading of indigo is a process of oxidation.
[152] Seyewetz, A., and Mounier, D., *Compt. rend.*, **185**, 1279 (1927); *Bull. soc. chim.*, **43**, 648 (1928); *Chem. Abs.*, **22**, 916 (1928).

Ometer.[153] The crystals were shown capable of sublimation and when recrystallized from chloroform were obtained as crystals of a different character but the same melting point as that of *o*-tolueneazo-β-naphthol. A thin layer of the powdered compound sublimed to only a very small degree at 45°C., the temperature reached in the irradiation, and it was not possible to obtain crystals as in the case of the dyed fabric. The cotton fabric suffered a loss of color due to this sublimation in the Fade-Ometer, but it did not change in color or become dull as it does when exposed in sunlight. Sublimation effects were observed also with cotton dyed with *o*-tolueneazo-α-naphthol and with combinations of Naphthol AS-BO and AS-RL with Fast Orange G base, but no crystals were formed on the surface.

Curtis[154] states that solutions of aniline green and magenta are not bleached when exposed to a quartz mercury arc. Neither are they bleached by the addition of 3-per cent hydrogen peroxide until the mixture is rayed. It was possible to exclude ozone as a cause of the bleaching. Holmes[155] reports that solutions of magenta, malachite green, methyl violet and crystal violet which had been decolorized by sulfur dioxide develop their original colors when exposed to ultraviolet rays of wave-lengths shorter than 3300A.

The photo-oxidation of many dyes by potassium dichromate was studied by Plotnikov.[156] Aqueous solutions of the following dyes were not affected: trypan blue, induline, dahlia, aniline green, malachite green, naphthol green, iodine green, nigrosin, trypan red, erythrosine, indigocarmine blue, gentian violet, Guinea green B and G, Brilliant Safranine, Aurantia, safranine, lithion carmine, carmine II, rose Bengal, Rhodamine B, Hofmann violet, methyl violet, crystal violet, cresyl fast violet. On the other hand, ethyl green, cyanin and naphthalene blue change very rapidly, both in light and darkness. Nile blue and cresyl blue 2BS are stable in darkness even on boiling, but in light change fairly quickly to bright red, fluorescent substances.

Tests for the Light-fastness of Dyes

The reproducible determination of the light-fastness of a dye or the relative light-fastnesses of a series of dyes requires the consideration of several factors. The distribution of the energy available at various wave-lengths in the light of the source employed for the test is of the utmost importance for the rapidity and reproducibility of the results. In some dyes, the absorption is predominantly in the visible; in others there are additional bands in the ultraviolet. Furthermore, the absorption spectrum and photochemical behavior of a dye in pure solution or in a collodion film may differ from that which it exhibits when applied to a fiber. In addition, the absorption of light by the fiber must be taken into account, since it may either lessen the amount of light available for the destruction of the dyestuff or it may cause photochemical changes in the fiber which result in the production of products which may hasten or retard the fading of the dye. The intensities of the radiations at various wave-lengths in sunlight vary extremely with the location at which the tests are conducted, with the time of year and with the amount of cloudiness, dust, smoke, etc. Variations in temperature, humidity, and the presence of acid fumes, also complicate the results of sunlight fading tests. As a result, it is difficult to secure reproducible results in successive tests at a given station, and far more so to make the results at one station compare with those obtained at another geographical location. For these reasons, exhaustive studies have been made by a Subcommittee on Light-fastness of the American Association

[153] Hibbert, E., *J. Soc. Dyers Colourists*, **44**, 300 (1928); *Brit. Chem. Abs.*, **B**, 854 (1928).
[154] Curtis, H. A., *J. Am. Chem. Soc.*, **42**, 720 (1920); *J. Chem. Soc.*, **118**, 342 (1920).
[155] Holmes, E. O., Jr., *J. Am. Chem. Soc.*, **44**, 1002 (1922).
[156] Plotnikow, J., *Z. Elektrochem.*, **32**, 13 (1926).

of Textile Chemists and Colorists[157] to find a substitute for sunlight whose fading action will have speed, similarity to the action of the sun, and a capacity for exact reproduction at different times and places. Similar investigations have been undertaken in other countries.[158] Recent workers have tended to emphasize the unsuitability of most artificial sources for giving results directly comparable with those of actual sunlight fading, since the effects in the latter case are predominantly due to absorption of visible rays, whereas the artificial sources most frequently advocated usually produce either disproportionately large amounts of the longer ultraviolet radiations of sunlight or even radiations of wave-lengths shorter than those available in sunlight.[159] Accordingly much effort has recently been expended in improving the sunlight test. Hibbert[160] observed that certain colors dyed on cotton and Cellophane exhibited very different fading rates when exposed to sunlight or to ultraviolet rays. The larger the proportion of short ultraviolet rays in the source employed, the greater the attack on the cellulose. This produces reducing substances which may affect the dye. Harrison[161] observed that in vacuum under a mercury arc, cellulose reduced flavanthrene and many direct colors, the cellulose being itself oxidized. In sunlight, however, the cellulose is less rapidly attacked, and this explains why direct colors fade much more slowly in sunlight. The direct colors are said not to fade in the absence of the fiber, and wool is not as powerful a reducing agent for them as is irradiated cellulose. On the other hand, Harrison found basic colors to fade usually by oxidation processes, although fading by reduction may occur under certain conditions. Thus it is apparent that the nature of the substrate, as well as the spectral energy distribution, is involved in determining the results of fading tests.

It has frequently been stated that deep shades are faster than pale shades. Barker, Hirst and Lambert[162] stated that measurements of the proportional losses of the predominant color in worsted fabrics dyed to different depths of shade with each of fifteen acid, mordant, and direct dyes, produced by sunlight and by light from a Fade-Ometer showed that the loss of color during fading was independent of the depth of the shade. Since the total color loss is the same for all shades, it is a much higher percentage of the total color in the pale than in the deep shades. Recently, however, attention has been called to the existence of a possibility that dyes exhibit a maximum sensitivity to light when present on the fibers at a certain concentration called the "mean critical tone." Pinte[163] believes that all comparative tests should be made at the previously determined "mean critical tone," since the fastness of a color improves the further it is from this value, whether toward zero, or 100. It is approximately 55 per cent for yellows, 45 per cent for oranges, 40 per cent for reds, and 35 per cent for violets, blues and greens.

[157] Cady, W. H., *Proc. Am. Assoc. Textile Chem. Colorists*, 225, 1925; *Am. Dyestuff Rept.*, **14**, 58; *Chem. Abs.*, **18**, 906 (1924). For general discussion on light-fastness tests, see Jameson, C. W., *Am. Dyestuff Rept.*, **21**, 306 (1932); Goodings, A. C., *Am. Dyestuff Rept.*, **24**, 663 (1935); Pestalozzi, S., *Zellstoff und Papier*, **17**, 53 (1937); *Chem. Abs.*, **31**, 3283 (1937); Déribéré, M., *Tiba*, **13**, 173, 175, 259, 329, 331, 415, 417, 481, 547, 549, 607, 687 (1935); Schupp, E., *Monatsh. Seide, Kunstseide*, **41**, 441, 488 (1936); Ris, H., *Klepzig's Textil-Z.*, **39**, 731 (1936); Rein, H., *Ibid.*, **39**, 732 (1936); Beil, A., *Angew. Chem.*, **49**, 905 (1936); Hirst, H. R., *J. Soc. Dyers Colourists*, **41**, 347 (1925); Merck, O., *Farben Ztg.*, **34**, 1117 (1929).
[158] Lantz, L. A., and others, *Fastness Committee, Society of Dyers and Colourists*, 52 pp., 1934; *Chem. Abs.*, **28**, 7538 (1934).
[159] Rein, H., *Angew. Chem.*, **47**, 157 (1934).
[160] Hibbert, E., *J. Soc. Dyers Colourists*, **48**, 251 (1932); *Chem. Abs.*, **27**, 192 (1933).
[161] Harrison, W., *J. Soc. Dyers Colourists*, **28**, 225 (1912).
[162] Barker, S. G., Hirst, H. R., and Lambert, P. N., *J. Soc. Dyers Colourists*, **43**, 264 (1927); *Chem. Abs.*, **21**, 3746 (1927).
[163] Pinte, J., *Chambre Commerce Roubaix Lab. recherches ind.*, No. **25**, 10 (1935); *Chimie et industrie*, **34**, 923; *Chem. Abs.*, **30**, 1234 (1936).

Humidity is also an important factor. Hedges[164] observed that the fading by a Hanovia mercury arc of wool patterns dyed with Ponceau RG, Acid Green G and Cyanin B under various conditions of humidity indicated an increased fading with increased humidity of the atmosphere surrounding the dyed patterns. The losses for these three dyes were for Ponceau RG at 52 and 100 per cent relative humidities, 1.5 and 4.9 per cent, for Acid Green G at 33 and 100 per cent, 11.2 and 21.7 per cent, and for Cyanin B, at 24 and 100 per cent, 23.8 and 41.0 per cent.

It is also important to agree upon the use of a definite method for determining the extent to which fading has occurred in a test. Many methods have been suggested. Gebhard[165] recorded the change of color, whether fading or change to another tint, by orthochromatic photography, using a light filter of the same color as the original dyeing. Appel and Smith[166] recorded the fading in the form of quantitative reflection measurements. Bravo[167] used a Pulfrich step photometer with that one of three spectral filters which most nearly coincided with the predominant color of the dye in making his observations. Mougeot[168] preferred a Toussaint photocolorimeter and believed "etalons" unsatisfactory. Niederhauser[169] recommended the use of a photocolorimeter and, in the exposure the Toussaint and Pinte "insolameter," which excludes dispersed daylight and measures the amount of light received by the illuminated materials. Probably the greater number of observers rely upon a simple visual comparison of the faded material with dyed patterns retained in darkness as standards. Hirst, in an earlier period,[170] indeed, considered such results as of more value than those obtained with the instruments then available.

Sunlight Tests. Much evidence has been accumulated as to the effects of variations of weather conditions on these tests; the data is so extensive that the original papers must be consulted. Barker and Hirst[171] investigated the effects on patterns on worsteds dyed with Victoria Blue and 85 other dyes, of sunlight during the months January to June in Leeds and in the country nearby, and also under five different cloud conditions. Full sunlight caused a fairly constant relative fading of Victoria Blue. Dull light had about one-tenth the effect of full sunlight. With Wardle, they charted the comparative sunlight values for different hours of the day for the six months included.[172] The value of the light for the total period of exposure could be expressed, by the aid of their graphs, in terms of what they considered a definite unit, one hour of June midday sun. For the variations of sunlight in the United States, and the differences between sunlight and the light of various artificial sources, see Anderson.[173]

Cady[174] found the angle of exposure to be important, the fading being greatest

[164] Hedges, J. J., *J. Soc. Dyers Colourists,* **43,** 261 (1927); Hill, L., *Ibid.,* 296; Cunliffe, P. W., *Ibid.,* **45,** 215 (1929); *Chem. Abs.,* **21,** 3746 (1927); **23,** 4824 (1929).

[165] Gebhard, K., *Farben. Ztg.,* **22,** 6 (1911); various methods have been discussed by Cunliffe, P. W., *J. Soc. Dyers Colourists,* **45,** 215 (1929).

[166] Appel, W. D., and Smith, W. C., *Proc. Am. Assoc. Textile Chem. Colorists,* 180 (1928); *Chem. Abs.,* **22,** 3048 (1928).

[167] Bravo, G. A., *Boll. ufficiale staz. sper. ind. pelli mat. concianti,* **8,** 50 (1930); *Chem. Abs.,* **24,** 2888 (1930); *Boll. ufficiale staz. sper. ind. pelli mat. concianti,* **9,** 210 (1931); *Chem. Abs.,* **26,** 2321 (1932).

[168] Mougeot, P., *Bull. soc. franç. elec.,* **5,** 965 (1935); *Chem. Abs.,* **30,** 4676 (1936).

[169] Niederhauser, *Klepsig's Textil. Z.,* **39,** 739 (1936); *Chem. Abs.,* **31,** 1623 (1937).

[170] Hirst, H. R., *J. Soc. Dyers and Colourists,* **41,** 347 (1925); *Brit. Chem. Abs.,* **1926B,** 43.

[171] Barker, S. G., and Hirst, H. R., *J. Textile Inst.,* **17,** 483T (1926); *J. Soc. Chem. Ind. Suppl.* 976 (1926).

[172] Barker, S. G., Hirst, H. R., and Wardle, G. C., *J. Soc. Dyers Colourists,* **43,** 324 (1927).

[173] Anderson, W. T., Jr., *Proc. Am. Assoc. Textile Chem. Colorists,* 273 (1928). Note also Appel, W. D., *Ibid.,* 275, and Cady, W. H., and Appel, W. D., *Ibid.,* 179 (1927).

[174] Cady, W. H., *Proc. Am. Assoc. Textile Chem. Colorists,* 225 (1925); *Chem. Abs.,* **20,** 668 (1926).

with horizontal exposures and less in order with 45° and with vertical ones. The angle of exposure is important only when total fading is considered; it has little effect on relative fading. Covering the samples with glass has effects which differ with different dyes. The effect of free circulation of air or the lack of it cannot be ignored. Continuous exposure produces different fading from that due to exposure only to the high cloudless sun. Direct sunlight has a different effect from skylight without sun. Exposures made in different localities show little variation in relative fading.

Barker and Hirst[175] described an exposure cabinet for protecting the patterns from dirt, soot and rain. As a transparent, protective screen they employed Vita glass (see Chapter 10). Cady and Appel[176] recorded the energy received by some of the samples with the aid of a barium photoelectric cell and automatic recorder. They found that approximately reproducible relative fadings could be obtained in a series of dyeings exposed in widely separated stations in the United States at different times in the year at an angle of 45° from the horizontal, facing south, between 9 A.M. and 3 P.M. on sunny days only, in a cabinet covered with a good grade of window glass approximately one-eighth inch thick. The cabinet was open at the sides and the distance between the glass and the samples not less than one-half rich. They felt that no artificial light source could be recommended. The quantity of radiant energy as recorded in some of the exposures did not correspond to the amount of fading produced. In later work embracing 1252 dyeings on cotton, wool, silk and weighted silk of 381 different coloring matters[177] they found the presence or absence of a glass cover to have a marked effect on the fading in only 4 per cent of the samples. Earlier observations by Pierce[178] had indicated that glass keeps out most of the active rays. Hirst[179] had suggested that dyes intended for outside purposes should be directly exposed to sun and weather and that those intended for inside indoor use should be exposed under glass. It would seem that the use of Vita glass would permit the fading of the small group of dyes not susceptible to the wave-lengths transmitted by glass without complicating the results in the case of other dyes by the use of radiations not present in the solar spectrum.[180] Appel and Smith[181] tested Corex, Vita and six other glasses on twenty samples determining the extent to which the fading was affected by the manner in which they change the distribution of the intensities at various wave-lengths. It was found that the visible and long-wave ultraviolet of sunlight were relatively more important in comparison with the shorter wave-lengths of sunlight than had been commonly supposed. As a result they considered window glass satisfactory for the standard sunlight test.

Hirst,[182] who favored the use of the usual five degrees of fastness selected as standards the following dyes, given in increasing order of fastness: 0.4 per cent Indigocarmine X (BDC). I. 1.5 per cent Ponceau RG (BDC). II. 2.75

[175] Barker, S. G., and Hirst, H. R., *J. Soc. Dyers Colourists,* **43,** 300 (1927); *Chem. Abs.,* **21,** 3747 (1927).

[176] Cady, W. H., and Appel, W. D., *Proc. Am. Assoc. Textile Chem. Colorists,* 179, 1927; *Chem. Abs.,* **22,** 319 (1928).

[177] Cady, W. H., and Appel, W. D., *Proc. Am. Assoc. Textile Chem. Colorists,* 217 (1929); *Am. Dyestuff Rept.,* **18,** 407; *Chem. Abs.,* **23,** 4824 (1929).

[178] Pierce, E. W., *Chem. Eng.,* 97 (1918); *Textile World J.,* Jan. 12, 1918.

[179] Hirst, H. R., *J. Soc. Dyers and Colourists,* **41,** 347 (1925); *Brit. Chem. Abs.,* **B,** 43 (1926).

[180] Griffith, I. O., and Jenkins, R. G., *J. Soc. Dyers Colourists,* **43,** 297 (1927) find plate glass as used in shop windows to transmit 90 to 95 per cent of the visible spectrum and a small proportion of the ultraviolet from 3500 to 3000A but scarcely any of that between 3000 and 2900A.

[181] Appel, W. D., and Smith, W. C., *Proc. Am. Assoc. Textile Chem. Colourists,* 180 (1928); *Chem. Abs.,* **22,** 3048 (1928).

[182] Hirst, H. R., *J. Soc. Dyers and Colourists,* **41,** 347 (1925); *Brit. Chem. Abs.,* **B,** 43 (1926).

per cent Azorubine (Sand.). III. 4.5 per cent Kiton Red S (CAC). IV. 2.5 per cent Chlorazol Fast Red FG (BDC). V. Indigo Full Shade or Natural Green B (C).[183] Tables of the German, English and American standards of dyes for light stability have recently been given by Wahl.[184] The standard wool dyes were tested at stations all over the world and were found to be of value in comparing the light effects available at various localities for testing other dyes simultaneously.

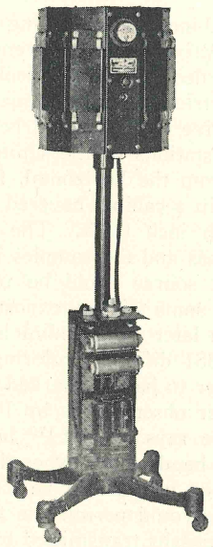


FIGURE 128.

Apparatus for Dye or Paint Testing.

Courtesy Cooper-Hewitt Electric Co.

Use of Artificial Sources. A number of early observers felt that the saving in time by and, they believed, greater reproducibility of the mercury arc as a source would more than compensate for any differences in fading which some dyes might exhibit under it.[185] Pierce believed that one hour under the mercury arc roughly paralleled an average day of exposure to sunlight. Apparatus of this type is commercially available (see Fig. 128) for both dye and paint testing. It consists merely of a circular cabinet about a vertical quartz mercury arc. The walls support removable panels to which the samples are attached. In comparing the action of the mercury arc with that of the sun, Scheurer,[186] who attempted to protect the dyes from any ozone formed, found that indigo resisted the mercury arc better than it did sunlight, although Benzo colors which were hardly faded by sunlight were materially changed by the mercury arc in 24 hours. After an extended study, Harrison[187]

[183] Note also Deady, W. F., *Proc. Am. Assoc. Textile Chem. Colorists,* 242 (1925); Appel, W. D., *Am. Dyestuff Rep.,* **27,** *Proc. Am. Assoc. Textile Chem. Colorists* P 15 (1938).

[184] Wahl, A., *Rev. gén. mat. color,* **40,** 140 (1936); **41,** 460 (1937). See also Cunliffe, P. W., *J. Textile Inst.,* **28,** 203 (1937). For a new blue fastness scale, see Müller, E., *Klepzig's Textil Z.,* **39,** 732 (1936); Rein, H., *Angew. Chem.,* **47,** 157 (1934). A standard should be adopted for interrelating fastness to light and to weather, according to Vendor, A., *Monatschr. Textil-Ind.,* **52,** 262 (1937); *Chem. Abs.,* **32,** 1458 (1938).

[185] Pierce, E. W., *Chem. Eng.,* 97, 1918; *Textile World J.,* Jan. 12, 1918; Flynn, O. R., *Am. Dyestuff Reptr.,* **12,** 837 (1923); Gebhard, K., *Farben Ztg.,* **22,** 6 (1911).

[186] Scheurer, A., *Bull. soc. ind. Mulhouse,* **80,** 324 (1911).

[187] Harrison, W., *J. Soc. Dyers and Colourists,* **28,** 225 (1912).

agreed not only that there are differences between the sun and the mercury arc effects but also that the effects are different with mercury arcs of high and of low intensity. Flynn[188] extended these results and also used a filter of 1.25 mm. of crown glass with the mercury arc. Fig. 129 illustrates the relative fading of dyes on cotton when exposed to sunlight, the direct and the filtered mercury arc. The dyes are represented as rectangular strips, the degree of fading being represented by the part of the strip cut out. The sunlight fading is at one end and

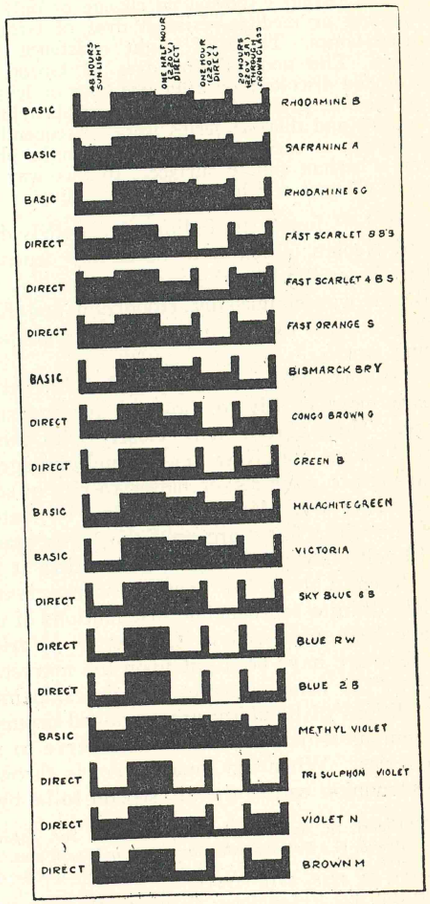


FIGURE 129.

Relative Fading of Dyes on Cotton.

the filtered mercury arc fading at the other. The intervening fadings represent the effect of one-half hour and one hour exposure by the direct mercury arc and show the reversal of the relative fastness between the direct and basic dyes when exposed to the unfiltered mercury arc. Under this source silk and wool appear to have less reducing action on dyes than has cotton.

[188] Flynn, O. R., *Textile World,* **53,** 25 (1923).

Iimori and Kitaoka[189] investigated the velocity of the bleaching of various dyes on cellulose acetate films before the mercury arc, but found it difficult to find one empirical equation which would express the behavior of every dye tested. Benzoic acid increased the rate of fading of methylene blue and disodium phosphate and calcium sulfate decreased it a little. For methyl violet, disodium phosphate, borax and quinine sulfate increased the rate slightly and calcium sulfate decreased it a little. Bravo[190] exposed a series of dyes on strips of filter paper at 50 cm. from a 2000 c.p. mercury lamp operated without a nickel oxide screen. The samples were ventilated to eliminate the possible influence of heat and ozone. One hundred and one dyes of the nitroso-, nitro- and azo- type were classified into four groups according to their resistance to bleaching. The very resistant dyes of Group I showed no change or only very slight changes after three hours. The resistant or medium-resistant dyes of Group II showed definite changes after two to three hours. Those of slight resistance (Group III) were altered in one to two hours. The non-resistant dyes of Group IV suffered intense changes in color or profound discoloration after one hour or less. Dyes of the nitro-, nitroso-, azo-, stilbene, pyrazolone, diphenylmethane and triphenylmethane, xanthene, acridine, quinoline, azine, oxazine and thiazine series were subsequently included. Bravo compared the percentage reflection at each of several wave-lengths photometrically with the corresponding values for a barium sulfate surface. In this way it was possible to study quantitatively the color changes which occur during fading.

Hill[191] found the fading of worsteds dyed with Indigocarmine X, Ponceau RG and Neolan Green B to be chiefly dependent on the ultraviolet of shorter wave-lengths emitted by the mercury arc. A tungsten arc lamp of the Osram Co. of Berlin was claimed by Hochheim and Knebel[192] to have a spectral distribution very similar to that of normal sunlight and therefore to be superior to the mercury arc.

It was early found by Gordon[193] that results with the violet carbon arc compare more closely to those of average sunlight than do those with the mercury arc. They agreed more closely with those of average sunlight than the results of Arizona and New Jersey sunlight agreed with each other. The white flame carbon arc gave rather better results in some cases but was only half as rapid as the violet arc. Mott and Bedford[194] stated that for equal line energy, the effect of the white flame arc on Solio paper was five to six times better than that of a 110-volt quartz mercury arc operating at four atmospheres at 60 arc volts.

Recently there has been great progress in the development of carbons which yield definite reproducible distributions of energy in various spectral regions; these have been discussed in Chapter 5. Various forms of apparatus employing the carbon arc have been put upon the market. In one form,[195] a number of "swatch boxes" in which samples of fabrics, paints, etc. may be exposed under definite conditions of humidity are arranged around a carbon arc. They are mounted on trunnions which are hollow and serve to supply conditioned air to all the boxes in series. When any swatch box is thrown down for inspection, the rotation of the trunnion causes the air stream to be by-passed around that box.[196]

[189] Iimori, S., and Kitaoka, K., *J. Chem. Soc. Japan*, **48**, 479 (1927); *Chem. Abs.*, **22**, 1855 (1928).

[190] Bravo, G., *Bol. ufficiale staz. sper. ind. pelli mat. concianti*, **8**, 50, 184, 2928 (1930); **9**, 210 (1931); *Industria Chimica*, **9**, 313, 461 (1934); *Brit. Chem. Abs.*, **B**, 711 (1934); *Chem. Abs.*, **25**, 2295, 3173 (1931); **28**, 4238, 6316 (1934).

[191] Hill, L., *J. Soc. Dyers Colourists*, **43**, 296 (1927); *Brit. Chem. Abs.*, **B**, 839 (1927). Gordon, H. B., *Textile Colorist*, **43**, 29 (1921).

[192] Hochheim, E., and Knebel, E., *Textilber.*, **6**, 912 (1925); *Brit. Chem. Abs.*, **B**, 437 (1926); *Chem. Abs.*, **20**, 669 (1926). See also Appel, W. D., *Proc. Am. Assoc. Textile Chem. Colorists*, 246 (1925); *Am. Dyestuff Rept.*, **14**, 882.

[193] Gordon, H. B., *Textile Colorist*, **43**, 29 (1921); *J. Soc. Chem. Ind.*, **40**, 149R (1921).

[194] Mott, W. R., and Bedford, C. W., *J. Ind. Eng. Chem.*, **8**, 1029 (1916). See also Cady, W. H., *Proc. Am. Assoc. Textile Chem. Colorists*, 42 (1925).

[195] King, F. A., British P. 309,726, April 2, 1928, to Kelvin, Bottomley and Baird Co.; *Brit. Chem. Abs.*, **B**, 461 (1929).

[196] For another form, see Hall, R. O., U. S. P. 1,969,606, to Ontario Research Foundation, and Bedford, E. F., *Silk J.*, **11**, No. 131, 38 (1935).

One of the most widely used types of commercial equipment is the Fade-Ometer (Fig. 130). In this, samples in metal specimen holders arranged in a circle are exposed to the light of a violet carbon arc enclosed in a 9200-PX glass globe. Ventilation is provided and the temperature is controlled by a thermostatically controlled blower. Textiles, papers and silks are generally tested between 98° and 104°F., but auto topping and similar materials are exposed at 140° to 150°F.

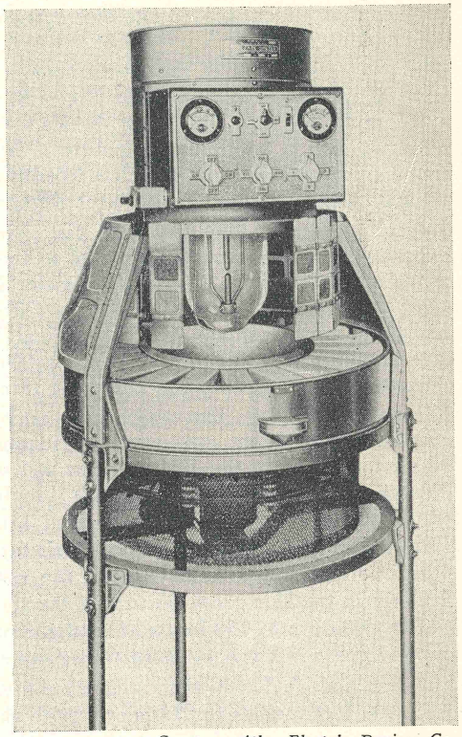


FIGURE 130.
Fade-Ometer, Type FDA.

Courtesy Atlas Electric Devices Co.

A relative humidity of 42 to 60 per cent at the specimens is produced by wicks in a water reservoir placed below the specimen chamber. The air coming in contact with the specimens must filter through 1600 sq. in. of saturated wicking. The light from the source employed is so near that of sunlight that 95 per cent of a series of 40 dyes tested by it faded exactly as in sunlight or acceptably close to the sunlight fading. The light is somewhat more intense than sunlight so that for textiles one hour in the Fade-Ometer is equivalent to 1.3 hours of summer sunlight. For lithographic inks, 2.33 Fade-Ometer hours are approximately equivalent to six hours of sun exposure. In general for dyed textiles, 48 Fade-Ometer hours are equivalent to 10 days of summer or 180 days of winter sunlight. For printing inks, paper, etc., the 48 hour test is equivalent to 20 average days of summer or 360 days of winter sunlight.

Barker and Hirst [197] determined the fading of woolen and worsted patterns dyed with about 60 acid, direct, vat and mordant dyes in Indian, Ceylon and English sunlight and in the light of a Fade-Ometer. They used a Lovibond tintometer for direct visual comparisons and for measurements of the fluorescence in filtered ultraviolet light. By comparison of the fluorescence patterns it was possible to tell which samples had been faded in England, which in the tropics and which by the Fade-Ometer. The results in the latter case did not agree with those of exposure of the patterns to direct sunlight. Also less fading occurred in the tropics than in England. The discrepancies were attributed to the differences in the humidity.

The progressive loss of the predominant color in worsteds dyed with Indigo-carmine X, Wool Green S, Neolan Green B, Acid Violet 6B, Magenta and Ponceau RG and Chlorazol Blue B in the Fade-Ometer are given by the expression $t=\alpha l^n$ in which t is the time of exposure in hours, l is the percentage loss of predominant color, α is a constant which depends on the dye and n is 1.9 or 2.0. The actual and calculated color losses differ slightly during the early stages of fading.

Appel [198] recently concluded that the change in reflectance of some dyeings on exposure to light is not proportional to the intensity of the incident radiation, since when the intensity of the Fade-Ometer light was cut to one-tenth, the time required to produce a definite fading in different dyes was anywhere from two to ten times that required at the original intensity. Similarly, lowering the relative humidity from 75 to 31 per cent retarded the rate of fading of some dyes by a factor of two, but failed to affect the rate of fading of others.

Kinsman [199] employs the carbon arc and believes an exposure of 64 hours to be roughly equivalent to one month of summer sunlight. From comparisons of the results produced by the Fade-Ometer and sunlight, Griffith, Brode and Robertson [200] conclude the former (Type LV) to be a satisfactory substitute for the latter. Peach, yellow and green pure dyed Tru-hu silk crêpe and yellow, blue and rose Peter Pan gingham were used in their tests. The blue gingham did not fade in either the sun or the Fade-Ometer; the rose gingham faded more in the sun, particularly in the blue-green portion of the spectrum. The yellow gingham faded only after exposure to 150 hours of sunlight or in the Fade-Ometer. The peach, yellow and green silk crêpes faded to the same extent with both sources.[201]

Luckiesh and Taylor [202] noted that 23 silk ribbons exposed to sunlight and skylight at 3900 foot-candles for 11 hours, or to skylight alone at 450 foot-candles for 40 hours, showed as much fading as those exposed to 500 foot-candles from tungsten lamps for 100 hours. Approximately equal degrees of fading will result from exposure to the tungsten-filament radiation for 100 foot-candle hours, skylight for 34, or sunlight and skylight combined for 74.[203]

[197] Barker, S. G., and Hirst, H. R., *J. Soc. Dyers Colourists*, **43**, 254 (1927); Barker, S. G., Hirst, H. R., and Lambert, P. N., *Ibid.*, 263; *Brit. Chem. Abs.*, **B**, 811 (1927); Barker, S. G., *J. Textile Inst.*, **18**, 313 (1927); *Chem. Abs.*, **22**, 2059 (1928).

[198] Appel, W. D., *Proc. Am. Assoc. Textile Chem. Colorists*, 194, 202, 1935; *Am. Dyestuff Rept.*, **24**, 306, 314 (1935); *Chem. Abs.*, **29**, 5276 (1935).

[199] Kinsman, S. T., *J. Oil and Colour Chem. Assoc.*, **12**, 274 (1929); *Brit. Chem. Abs.*, **1930B**, 51.

[200] Griffith, M. E., Brode, W. R., and Robertson, H., *Ohio Agr. Sta. Bimonthly Bull.*, **169**, 143 (1934); *Chem. Abs.*, **28**, 7021 (1934).

[201] For a summary of early work on the suitability of various sources, see Hadfield, I. H., *J. Textile Inst.*, **18**, 527T (1927).

[202] Luckiesh, M., and Taylor, A. H., *Am. Dyestuff Rept.*, **14**, 613, 636 (1925); *Chem. Abs.*, **19**, 3597 (1925).

[203] For observations on the effect of ultraviolet on certain dyes, see McEwen, J. L., *Am. Dyestuff Rept.*, **21**, 337 (1932).

Various Types of Dyestuffs. Heermann [204] proposed to classify dye and textile fiber systems into four groups according to their susceptibility to light of various wave-lengths. These classes, termed "micro," "macro," "homo" and "mesotropic," are, respectively, most susceptible to light of short wave-lengths, long wave-lengths, all wave-lengths and to the ultraviolet rays of sunlight. Auramine, which is notoriously not fast to sunlight, resists short ultraviolet rays rather well.

In azo dyes,[205] the naphtha dyes having a hydroxyl group in the 2-position are superior to those in which it is in the 1-position. The exceptions are 1-naphthol-4-sulfonic acid, which is comparatively fast, and 2-naphthol-3,6-disulfonic acid, which is fugitive. The presence of two sulfonic acid groups in the naphthol nucleus does not decrease the fastness of the dyestuff. *p*-Sulfanilic dyes are more affected than *o*-sulfanilic acid dyes but less than *m*-sulfanilic acid dyes. The degree of darkening is little influenced by the presence or position of the sulfonic acid group in the benzene nucleus, although there is slightly less darkening in the *o*- and *p*-sulfanilic acid dyes. The combined effect of fading and darkening, which gives the total effect of light on these dyes, indicates that the *o*-sulfanilic acid dyes are superior to those made from aniline and *p*- and *m*-sulfanilic acids.

Kinsman [206] classifies lakes into five arbitrary groups according to the effects of light upon them. Group I, no perceptible alteration after one month in summer sunshine; II, slight loss; III, distinct loss in depth or alteration of shade; IV, distinct loss or alteration after 14 days; V, practically complete bleaching after one week. In practice, however, an accelerated test with a carbon arc was employed. Lakes belonging in the respective classes were as follows: I, Alizarin-red, aluminum calcium phosphate lake; II, Permanent-red 4B, calcium salt; III, Lithol-red R, barium salt; IV, Eosin YS, lead salt, barium sulfate base; V, lakes of fastness less than that of eosin. The carbon arc readings of these types are; unbleached after 240 hours, practically unbleached after 120 hours, bleached after 60 hours, bleached after 34 hours, bleached in less than 34 hours.

Wool patterns heavily dyed with Naphthol Yellow S, after exposure to sunlight until extensive browning had occurred, responded to a color test for 2-nitro-4-amino-α-naphthol-7-sulfonic acid, indicating the browning to be the result of photoreduction.[207] The slow bleaching of annatto solutions by air is much more rapid in light.[208]

If dyed Celanese is treated with such organic bases as dimethylaniline or diethylaniline, which absorb wave-lengths shorter than about 3400A, the light fastness of certain colors is improved. Colors strong in nitro- groups however, seemed to be deteriorated by this treatment.[209] The best protection for airplane wings is to dye the dope with spirit black.[210]

Colored Papers. Very similar methods are employed in testing the fading of dyes applied to paper. Appel and Bentzen [211] recommend the Atlas Fade-

[204] Heermann, P., *Chem. Ztg.*, **48**, 813, 834 (1924). For recent reviews see H. Niimiya, *Chem. Rev. (Japan)*, **3**, 401 (1937); Pierce, E. W., *Rayon Textile Monthly*, **19**, 249, 263 (1938); Volz, K., *Spinner u. Weber*, **56**, No. 34, 43, 53 (1938).

[205] Griffith, M. E., *Ohio Agr. Expt. Sta., Bull. No.* **548**, 80 (1935); Griffith, M. E., and Brode, W. R., *Ibid., Bull.* **565**, 3 (1936); *Am. Dyestuff Rept.*, **26**, 90 (1937); *Chem. Abs.*, **30**, 1565 (1936); **31**, 1211 (1937).

[206] Kinsman, S. T., *J. Oil and Colour Chem. Assoc.*, **12**, 274 (1929); *Chem. Abs.*, **24**, 737 (1930).

[207] Hodgson, H. H., and Smith, E. W., *J. Soc. Chem. Ind.*, **56**, 108T (1937); *Chem. Abs.*, **31**, 4500 (1937).

[208] Barnicoat, C. R., *J. Dairy Research*, **8**, 61 (1937); *Chem. Abs.*, **31**, 3581 (1937).

[209] Ellis, G. H., *Chem. Age*, **13**, 470 (1925); *J. Soc. Chem. Ind.*, **44**, 1093 (1925).

[210] First Report Fabrics Coördinating Research Committee, Dept. Sci. Ind. Research, 10 (1925); *Chemical Age (London)*, **13**, 331, 397 (1925).

[211] Appel, W. D., and Bentzen, T., *Paper Trade J.*, **88**, No. 9, 42 (1929); *Chem. Abs.*, **23**, 3095 (1929); Dalen, G., and Wilke, P., used the mercury arc, *Papier-Fabr.*, **26**, 199; *Chem. Abs.*, **22**, 2272 (1928).

Ometer, particularly the type equipped with a fan to prevent excessive heating of the sample. Grundy,[212] who also approved the method, noted that the exposed dyeings should be allowed to cool a short time before comparing the colors, since a slight change in shade may be due to the heat of the arc, rather than to fading. It did not seem possible to make standard numerical specifications for the light-fastness of colors on all qualities of paper. No basic colors were found which had sufficient fastness to receive consideration for the production of fast-to-light shades. With the ordinary type of soluble synthetic dyestuffs generally applied on paper, it seemed impossible to obtain fast shades on furnishes containing even small quantities of brown wood. The most suitable furnishes for fast-to-light shades are bleached sulfite, bleached soda, esparto, bleached rag, and under certain conditions unbleached sulfite, either individually or in mixture.

Loading materials affect the light fastness of dyes in paper,[213] partly because of the alkalinity of the filler. The pH of filled or unfilled papers is generally reduced by exposure to sunlight. Papers of lower pH values are the more easily faded. Dyes which are fast to light are generally acid resistant.

Riesenfeld and Hamburger [214] employed the time of exposure to a standard ultraviolet source required to produce a definite change in fluorescence as a measure of the relative light fastness of dyed papers.

Harrison [215] did not approve the use of the Grant method of following the reduction of fluorescence on irradiation, but could find no suitable inexpensive daylight lamp for comparing the samples. He proposed the use of bleached sulfite pulp, colored with graduated amounts of fast dyes, including the Chlorantin colors, or using one amount with additions of hexadecylpyridinium bromide to decrease the fastness. The sheets were then exposed to direct sunlight for 6, 12, 24, 48 and 96 hours and compared with controls or with irradiated controls without the addition of the deteriorating agent. He measured the light intensity to which the sample was exposed by an actinometric paper and a wedge-shaped slide transmitting graded amounts of light. This, when laid over a standard colored sheet, simulates the effect of graded bleaching. With this method, the best results were obtained with a pure rag paper, sized with 2 per cent rosin and 4 per cent alum, and dyed with Acid Rhodamin 3R.

Inks. Proposals have been made to employ ultraviolet radiations for testing inks by measuring the color of streaks on paper after exposure for two weeks to sunlight or for a shorter period to ultraviolet light.[216] The Bureau of Standards [217] recommended an exposure of 48 hours to ultraviolet light. A comparison streak of a standard ink was simultaneously exposed. Turner [218] classified about fifty pigments into four groups according to their light fastness in printing ink.

Tests by Mitchell [219] did not substantiate the claim that ultraviolet fluorescence tests can be used for the differentiation of different types of inks or for the determination of their ages.

[212] Grundy, J. G., *World's Paper Trade Rev.*, **101**, 1240, 1242, 1280, 1399, 1442 (1934); *Paper Maker and British Paper Trade J.*, **88**, No. 1, 138 (1934); *Chem. Abs.*, **28**, 7010 (1934).

[213] Pestalozzi, S., *Zellstoff u. Papier*, **15**, 496 (1935); *Chem. Abs.*, **30**, 1558 (1936).

[214] Riesenfeld, E. H., and Hamburger, T., *Papier-Fabr.*, **29**, 164 (1931); *Brit. Chem. Abs.*, **B**, 625 (1931).

[215] Harrison, H. A., *Papier-Fabr.*, **34**, *Tech. Teil*, 321, 329 (1936); *Chem. Abs.*, **31**, 856 (1937); *Paper-Maker, TS* 54 (1936); *Chem. Abs.*, **31**, 2428 (1937); *Svensk Papperstidn.*, **39**, 352 (1936).

[216] Rupert, F. F., *Ind. Eng. Chem.*, **15**, 489 (1923); *J. Soc. Chem. Ind.*, **42**, 612A (1923).

[217] *Bureau of Standards Circular* **95** (1920).

[218] Turner, J. S., *Am. Ink Maker*, **14**, No. 1, 19 (1936); *Chem. Abs.*, **30**, 5817 (1936); Deeney, J. J., *Am. Ink Maker*, **11**, No. 2, 9, 23; No. 3, 13 (1933); *Chem. Abs.*, **27**, 5557 (1933).

[219] Mitchell, C. A., *Analyst*, **55**, 746 (1930).

Ink on freshly printed sheets dries faster when exposed at a distance of six inches from a mercury arc than in diffused lights, especially at higher temperatures.[220]

In making hectograph copying pads, a gelatinous mass (gelatin, water and glycerol) is treated with a minute proportion of a light-sensitive tanning agent such as ammonium dichromate and subjected to the action of ultraviolet light to effect tanning.[221]

Fluorescence Tests of Dyes. Hirst and King [222] found that certain Indigosol dyeings on wool showed in ultraviolet light a strong violet fluorescence on the original dyeing, but not on portions which had been exposed to light for some weeks. They suggested that the fluorescence might indicate incomplete oxidation and incomplete development since its intensity varied when different oxidizers were used. The method also could be used for indicating the degree of exhaustion of the dye-bath and was thought of value in the control of this type of dyeing. Kummerer [223] tabulated the fluorescence colors in ultraviolet light of variously dyed fabrics. The determination of fibers by their fluorescence colors is, according to Sommer,[224] subject to distinct limitations. For example, the dye present may entirely obscure the fluorescence color of the fabric or even lead to false conclusions. No certain distinction could be made between dyed flax and hemp. Bleached linen and cotton could not be distinguished nor could mohair and wool. Egyptian cotton is readily determined, as is dyed wool intended as a substitute for camel hair. Oil spots on fabrics are especially distinct. Alkali or acid damage to wool is not determinable by this method. After sulfite cellulose pulp has been exposed to a bright light it cannot be distinguished in this manner from soda pulp. The method cannot be used to identify coloring matters, according to Radley.[225]

Textile Printing [226]

Haendel [227] described a process in which woven and knitted or plaited fabrics, leather and other materials are dyed or figured by treating them with light-sensitive compounds and subsequently exposing them to the action of light. Substances may be used which form dyes when exposed to light, such as mixtures of a sulfonated diazo- compound, *e.g.*, sodium phenyldiazosulfonate and an azo- component such as aniline hydrochloride. Light-sensitive substances which lose their capacity to form dyes when exposed to light may be used.

Designs may be applied to yarns, bands or fabrics of non-animal origin in a continuous operation involving application of a metal compound convertible photochemically into a compound in which the valence of the metal is different, exposure to ultraviolet light passing through a pattern, washing, conversion of either

[220] Brown, R. A., *Am. Ink Maker*, **9**, No. 3, 21 (1931); *Chem. Abs.*, **25**, 3500 (1931). The carbon arc is used by Arend. A. G., *Process Engraver's Monthly*, **44**, 173 (1937).

[221] Whitmore, W. B., U. S. P. 2,024,408, Dec. 17, 1935, to Ditto, Inc.; *Chem. Abs.*, **30**, 1156 (1936).

[222] Hirst, H. R., and King, A. T., *J. Soc. Dyers Colourists*, **43**, 266 (1927); *Chem. Abs.*, **22**, 2276 (1928); *J. Textile Inst., Special No.*, **18**, 369T (1927); *Chem. Abs.*, **22**, 2061 (1928).

[223] Kummerer, L., *Melliand Textilber.*, **9**, 415 (1928). Sisley, P., [*Chimie et industrie, Special number 508* (March 1932)] gives data on 1200 dyes.

[224] Sommer, H., *Melliand Textilber.*, **9**, 753 (1928); *Chem. Abs.*, **22**, 4825 (1928); compare de Buda, G., *Cuir tech.*, **21**, 98 (1932); *Chem. Abs.*, **26**, 3115 (1932).

[225] Radley, J. A., *J. Soc. Dyers Colourists*, **53**, 376 (1937); *Chem. Abs.*, **32**, 364 (1938).

[226] In the decoration of fabrics by the reducing action of light on silver salts, Michels, M., [German P. 441,690, May 4, 1926; *Bull. soc. ind. Mulhouse*, **94**, 124, 135 (1928); *Chem. Abs.*, **22**, 2468 (1928)] uses as a mordant for all basic dyes, a material formed from complex copper compounds.

[227] Haendel, W., British P. 309,166, April 7, 1928; *Chem. Abs.*, **24**, 509 (1930).

the altered or unaltered portion of the metal compound into a substance which cannot be washed out, washing and drying.[228]

In an example, linen is passed through potassium dichromate solution, then over a rotary stencil containing one or more carbon arc lamps or mercury discharge tubes, treated with sodium alizarine sulfonate solution after passing through water, washing and drying.[229]

Freytag [230] showed that ultraviolet irradiation of solutions containing aniline hydrochloride and suitable oxidizing agents and catalysts as used in aniline black dyeing markedly accelerates the formation of the aniline black pigment. Satisfactory reproduction of images may be obtained by impregnating paper or cotton fabric with a 1- to 25-per cent solution of aniline hydrochloride containing five drops of aqueous 4-per cent potassium ferricyanide and 18 to 24 drops of 10-per cent aqueous sodium chlorate per 30 cc., covering with a photographic negative and exposing for fifteen minutes to ultraviolet light, and washing out unchanged aniline with water.

Similarly, solutions of either of the phenylenediamines produce a yellow or brown color formed by oxidation of the base. The naphthylamines behave in an analogous manner.[231] The process is assisted by the presence of about 1 per cent of an alkaline nitrate in the naphthylamine bath. With β-naphthylamine, the process is very rapid and will take place even in sunlight.

Freytag and Müller [232] also employed 2-benzyl pyridine, which becomes deep brown on exposure to light. Radiation of 2000 to 4000A converts it into a green dye. The compound is applied in 96-per cent alcohol and the solvent evaporated before making the exposure to light through a negative. The excess of unaltered compound is removed with dilute hydrochloric acid. The fastness of the photopyridine colors can be improved by coupling with diazotized bases.[233] After exposure for thirty to forty-five minutes at 30 to 50 cm. from a quartz lamp, the sample is passed through a boiling acid bath containing two to three per cent of a primary aromatic amine. The color thus obtained lacks fastness, but this may be improved by treating it without washing with a solution of a diazonium salt of an aromatic base. There is considerable change in the color.

Benzidine and tolidine on irradiation in the presence of sodium nitrate are oxidized on the fiber to fast dyes.[234] The samples of cotton and artificial silk so treated are coffee-brown with benzidine and yellowish-brown with *o*-tolidine. A number of amino-naphtholsulfonic acids have also been used.[235] The most suitable substances are the pyridines and the aniline salts of 8-nitro-1-naphthalenesulfonic acid. The best results are obtained when the exposures are made in a damp atmosphere.

Stabilized isodiazotate solutions [236] of aniline, *p*-brom- and *p*-iodo- aniline, etc.

[228] British P. 380,208, April 23, 1931, to N. V. Phillips Gloeilampenfabrieken; French P. 768,261, Aug. 3, 1934; *Chem. Abs.*, **27**, 3087 (1933); **29**, 621 (1935).

[229] For a general discussion of printing by photochemical processes, see Weickart, F., *Monatsh. Seide, Kunstseide*, **38**, 474 (1933).

[230] Freytag, H., *Melliand. Textilber.*, **13**, 144 (1932); *Chem. Abs.*, **27**, 1834 (1933).

[231] Freytag, H., *Phot. Korr.*, **69**, 184 (1933); *Chem. Abs.*, **28**, 7538 (1934).

[232] Freytag, H., and Müller, A., *Monatschr. Textilind.*, **48**, 239, 273 (1933); *Chem. Abs.*, **28**, 5245 (1934).

[233] Freytag, H., *Monatschr. Textilind.*, **48**, 107, 130 (1933); *Chimie et industrie*, **31**, 621; *Chem. Abs.*, **28**, 3590 (1934).

[234] Freytag, H., and Preiss, S., *Monatschr. Textilind.*, **49**, 209, 231 (1934); *Chem. Abs.*, **29**, 2362 (1935).

[235] *Monatschr. Textilind.*, **49**, 262 (1934); *Chem. Abs.*, **29**, 2362 (1935); *Phot. Korr.*, **71**, 52 (1935).

[236] Oddo, G., Indovina, R., Albanese, G., and Amatore, G., *Gazz. chim. ital.*, **65**, 939 (1935); *Chem. Abs.*, **30**, 3792 (1936).

again acquire the power of coupling after thirty minutes of exposure to sunlight, ultraviolet light or an ordinary incandescent lamp. This is of importance in the dyeing and printing of textiles, since it is unnecessary to treat the salts with hydrochloric acid to form diazonium salts and to couple these with alkaline β-naphthol or other phenols, or with a base, but only to expose the solutions with the other azo- component to heat, sunlight or ultraviolet light. It may also be of importance in negative diazo-printing. It was found possible with the halogenated bases easily to reproduce not only the image of any object impenetrable to sunlight, but also the colored image of the negative obtained by the ordinary photographic process.[237] The effect is not observed with *o*-toluidine, 1,3,4-xylidine, pseudocumidine and mesidine. Acidification of the alkaline coupling solution of diazotized aniline and acetamide gave a colorless precipitate which when dried rapidly in darkness was found to have the composition and molecular weight of acetylphenyltriazene. The crystals became reddish yellow in diffused light and after two weeks were a beautiful dark red. During this process the melting point dropped from 101 to 96°C.[238]

Cloth treated with certain vat dyes and dried may also be printed under a negative until the desired oxidation is complete, after which the unoxidized portion of the dye is removed by a boiling soap solution.[239] The dyes sensitive to ultraviolet include Indigosol Orange HR, Scarlet HR and Pink HR. Indigosol 4B and HB are less sensitive to sunlight.

Photographic Papers

In obtaining photographic images, Gay [240] mixed light-sensitive diazo- compounds with O-acyl derivatives of the phenols or naphthols, used as coupling components in development. The phenols or naphthols are liberated by development with ammonia gas or a dilute alkaline bath and a colored positive image is obtained.

For diazotypes, Kalle & Co.[241] use a diazo- compound capable of self-coupling in alkaline media applied in neutral or acid solution to the support. After exposure under a positive, the print is developed with gaseous ammonia. Suitable diazo- compounds are those from H-acid, 3-amino-6-N-piperidinobenzoyl-H-acid and 2,7-aminonaphthol.

Spencer [242] states that diazo- compounds for photographic papers should be sufficiently sensitive to light, and stable toward heat, mechanical shock, and to the paper base upon which they may be coated in sufficient concentration by the use of an inert solvent. They should couple readily with amines and phenolic compounds to give dark-colored substances insoluble in water and stable to light. The decomposition products should not interfere with the color or stability of the image. The following types of paper are possible: (a) the diazo- compound is decomposed by light and is developed by application of an alkaline coupler which reacts only with the unchanged diazo- compounds; (b) the diazo- compound and coupler are coated together, but reaction is prevented by the presence of an organic

[237] Oddo, G., and Indovina, R., *Gazz. chim. ital.*, **65**, 1037, 1099 (1935); *Chem. Abs.*, **30**, 4830 (1936).

[238] Oddo, G., and Algerino, A., *Ber.*, **69B**, 279 (1936); *Chem. Abs.*, **30**, 3418 (1936). For a discussion of visible light effects in certain phenyldibenzoxanthrenium dyes, see Dilthey, W., and Quint, F., *Ber.*, **69B**, 1575 (1936).

[239] Cowper, W., *Dyer, Calico Printer*, **58**, 117 (1927); *Chem. Abs.*, **22**, 1045 (1928).

[240] Gay, E., British P. 282,894 and 283,274 (1926); *Brit. Chem. Abs.*, **B**, 173 (1928).

[241] British P. 297,363, Aug. 19, 1928, to Kalle and Co.; *Brit. Chem. Abs.*, **B**, 350 (1930).

[242] Spencer, D. A., *Phot. J.*, **68**, 490 (1928); *Brit. Chem. Abs.*, **B**, 73 (1929).

acid, such papers being developed by weak alkali solutions or ammonia vapor; (c) the diazo- compound is coated with a coupler in an unreactive state, *e.g.*, as an additive compound, development being effected by breaking up the additive compound by heat, ammonia, etc.; (d) the diazo- compound is decomposed by light into a substance which will react with the original diazo- compound either on keeping or in the presence of alkali.

A combination of boric acid and an organic acid (citric, tartaric) is more efficient than the organic acid alone in preventing the premature formation of coloring matters in diazo- papers in which the coupling agent and the diazo- compound are applied together.[243] A suitable coating mixture is: stannic chloride double salt of 4-diazo-1-dimethylaniline, 22, boric acid, 20, tartaric acid, 50, phloroglucinol 2 and water 1000 parts. Preservation by depriving the surface of moisture during the preparation is also described.[244]

Neuroth[245] prepared light-sensitive layers by bringing aryl azides onto a support together with phenols, aromatic amines or aminophenols. Development of the exposed layer is effected by washing out the unreacted azide or by rendering it inactive by reduction.[246]

Schmidt and Spietschka[247] described the manufacture of light-sensitive paper from diazo- compounds of aminonaphtholcarboxylic acids, such as 1-diazo-2-hydroxy-3-naphthoic acid in sodium hydroxide. If exposed beneath a negative and washed with water, a blue-black print on a pure white ground is obtained. Schmidt and Zahn[248] add a compound other than a dye showing strong ultraviolet absorption, as sodium 6-phenyl-2-aminopseudo aziminobenzene-3,4′-disulfonate, to inks, or crayons for making drawings from which blue prints are to be prepared, in order to secure clearer reproduction.

Miscellaneous Processes. In a photographic method for the reproduction of natural wood grains, the softer parts of the wood are removed by chemical and mechanical means. The pattern is then fixed on a photographic plate from which the printing surface is produced. The treated wood may be illuminated by ultraviolet light for reproduction or may be directly printed by x-rays.[249]

Beebe[250] described a compound adapted for reproducing designs on metal, glass, etc. which comprises a varnish containing a light-sensitive oil (tung) and an accelerator (iodine) which serves to accelerate the action of light on the varnish for photographic purposes.

On the assumption that cellulose products as ethers or esters, papers, artificial soaps, etc., on exposure to ultraviolet light become permeable to gases, vapors or liquids, Kleiner,[251] patented a method for the production and reproduction of pictures or designs by visible or invisible rays.

[243] British P. 294,247, July 16, 1928, to Kalle & Co.; *Brit. Chem. Abs.*, **B**, 1033 (1929).

[244] N. V. Phillips' Gloeilampenfabrieken. French P. 794,590, Feb. 20, 1936; *Chem. Abs.*, **30**, 5137 (1936).

[245] Neuroth, H., German P. 510,165, Oct. 22, 1929, to Kalle & Co.; *Chem. Abs.*, **25**, 886 (1931).

[246] See also Werner, G., U. S. P. 2,063,832; *Chem. Abs.*, **31**, 620 (1937); Alink, R., U. S. P. 2,083,285; *Chem. Abs.*, **31**, 5285 (1937).

[247] Schmidt, M. P., and Spietschka, W., German P. 470,088, Dec. 11, 1927, to Kalle & Co.; *Chem. Abs.*, **25**, 466 (1931).

[248] Schmidt, M. P., and Zahn, R., German P. 517,159, July 24, 1926, to Kalle & Co.; *Chem. Abs.*, **25**, 2066 (1931).

[249] British P. 308,373-4-5-6, March 22, 1928, to Masa G.m.b.H. zur Herstellung künstlicher Oberfläche; *Chem. Abs.*, **24**, 32 (1930). See also for another process, R. R. Tanner, U. S. P. 2,127,944, Aug. 23, 1938; *Chem. Abs.*, **32**, 7840 (1932).

[250] Beebe, M. C., U. S. P. 1,574,356-7-8-9, Feb. 23, 1926; *Chem. Abs.*, **20**, 1362 (1926).

[251] Kleiner, S., British P. 413,095, April 26, 1933; *Chem. Abs.*, **29**, 417 (1935).

Polden[252] employs light or ultraviolet radiations or electric currents at superatmospheric pressures to accelerate the bleaching of tortoise shell and similar natural materials by bleaching agents that yield nascent oxygen, such as hydrogen peroxide.

[252] Polden, D. C., British P. 429,524, May 31, 1935; *Chem. Abs.*, **29**, 7531 (1935).

Chapter 33

Miscellaneous Applications of Ultraviolet Light

An application of the polymerization of oils by ultraviolet light is to be found in the production of patent leather. It has been claimed that the exposure of the varnished surfaces to the action of a mercury-vapor lamp gives the same result in one and one-half hours as is obtained by several days of exposure to sunlight. The method is not, however, widely used.

One process is carried out in an atmosphere containing ammonia derivatives, nitrogen, hydrogen or other neutral gases,[1] or in an exhausted chamber. The leather is carried on frames in the chamber, quartz lamps being arranged between the frames.[2] Lumbard[3] claims that better results are obtained if the extreme ultraviolet rays are filtered out.

An apparatus for the treatment described by Priest,[4] comprises a frame arranged on bearings which serves as a support for the hides which are to have their varnished surfaces exposed to the direct action of the ultraviolet rays. The action of the rays from a series of quartz lamps vertically arranged in the center of the revolving frame may be supplemented by the action of ozone.

Stoeckly[5] used ultraviolet rays produced by a high-frequency spark discharging thirty to sixty times per second, each spark consuming about 0.7 kilowatt. Prior to the use of artificial ultraviolet sources, the stock coated with the linseed oil varnish mixture was exposed to the direct rays of the sun for eight to ten hours. Such drying was greatly retarded by a humid atmosphere. Dinsley and Pulman[6] suggested subjecting leather to the ultraviolet rays prior to enameling it. Other patents dealing with structural features of the apparatus employed are due to Hughes,[7] and to Elliott.[8]

The kind of plasticizer is of primary importance in determining the rate of deterioration of nitrocellulose films in artificial leather if embrittlement and insolubilization of the surface on exposure to light are to be avoided.[9] Anderson and Lamb[10] studied the properties of films containing various plasticizers, added to the extent of 0.25 to 2.0 per cent to films from a 3-per cent solution of Cotton 8A (nitrocellulose) in equal parts of butyl acetate and butyl alcohol. The films were formed by flowing on glass and exposing to the mercury arc. Of the eight plasticizers studied, "Sipaline AOM" (dimethylcyclohexyl adipate) gave the best results as regards flexibility and durability on exposure to ultraviolet light. Triacetin is also recommended for leather which requires much stretching.

[1] Heyl, C., British P. 113,622, Feb. 21, 1918; Swiss P. 76,436, Dec. 17, 1917; British P. 113,620, Feb. 20, 1918.

[2] See also Swiss P. 77,117 and 77,378; Dutch P. 1,970; Danish P. 22,258 and 22,269; Hintz, E., *J. Soc. Chem. Ind.*, **37**, 709A (1918); *Chem. Abs.*, **12**, 1935 (1918); U. S. P. 1,269,931, June 18, 1918.

[3] Lumbard, V. G., *J. Am. Leather Chem. Assn.*, **10**, 86 (1915); *cf.* Lattey, W. T., *J. Oil and Colour Chem. Assoc.*, **9**, 45 (1926); *Brit. Chem. Abs.*, **B**, 377 (1926).

[4] Priest, G. W., U. S. P. 1,262,977, April 16, 1918; *J. Soc. Chem. Ind.*, **37**, 343A (1918).

[5] Stoeckly, J. J., British P. 148,454 and 149,334, 1920; *Chem. Abs.*, **15**, 329, 450 (1921).

[6] Dinsley, A., and Pulman, A. O., British P. 190,781, Sept. 23, 1921; *J. Soc. Chem. Ind.*, **42**, 193A (1923).

[7] Hughes, W. A., U. S. P. 1,747,301, Feb. 18, 1930, to Cooper-Hewitt Electric Co.

[8] Elliott, E. L., U. S. P. 1,702,043, Feb. 12, 1929; see also Brophy, J. J., U. S. P. 2,020,296; British P. 452,618, Oct. 26, 1935; *Brit. Chem. Abs.*, **B**, 1109 (1936).

[9] Genin, G., *Halle aux cuirs*, **67**, (1932); *Chem. Abs.*, **26**, 3136 (1932).

[10] Anderson, H., and Lamb, M. C., *Cuir tech.*, **23**, 130 (1934); *Chem. Abs.*, **28**, 5999 (1934).

Ultraviolet rays shorter than 3000A rapidly darken leather. This property can be used to produce designs on leather by the aid of stencils or Uviol glass photographic plates.[11] The darkening is caused by an iron-tannin compound. Light activates or frees both tannin and iron. Inorganic or organic compounds can be used to increase the depth and permanency of the designs or to alter their shade.

All vegetable-tanned leathers darken on exposure to light, frequently with a loss of strength, but[12] this is most marked in leathers tanned with catechol tannin. Attempts to find an effective inhibitor have been unsuccessful. The presence of water is necessary for darkening in ultraviolet light.

Fluorescence analysis methods have found application in leather chemistry.[13] Cuccudoro[14] believed it possible by such methods to assist in distinguishing between the various components of raw hide, that is, collagen, keratin, bloody tissues, and tanning materials. They also were found useful in determining the depth of penetration of vegetable tannins and the saturation of the hides with such materials and also in the examination of finished leather for indications as to the manufacturing processes which had been employed.[15]

The absorption spectra of solutions of various tanning materials have been measured by de la Bruère.[16]

The use of the ultraviolet microscope, which combines increased resolving power with the advantages of fluorescence, is finding application in the study of animal skin.[17]

Petroleum Products

Absorption Studies. Crude petroleum oils are characterized by absorption bands with maxima at about 3000, 2800, 2650, 2420 and 2400A due probably to cyclic hydrocarbons.[18] Transformer oils of various origins cannot be distinguished by ultraviolet absorption spectra. Aging of the oils merely decreases the sharpness of the bands.[19]

It has been stated that benzene, xylene and toluene can be readily determined in gasoline by ultraviolet absorption studies. Relatively little has, however, been written regarding the absorption of light by various petroleum products.[20] Schou and Bendix-Neilsen[21] find the absorption of a band at 2730A in samples of liquid paraffin parallels the results of the sulfuric acid test for organic impurities.

Mineral oils dissolved in various solvents change color on exposure to light according to the nature of the solvent.[22] Carbon tetrachloride, chloroform and amyl alcohol are the most active, but no changes take place in acetone and ether. In the absence of air, the discoloration is probably due to soluble polymerization products.

[11] Freytag, H., *Collegium*, 161, (1932); *Chem. Abs.*, **26**, 3955 (1932); French P. 707,490.

[12] Woodroffe, D., *J. Internat. Soc. Leather Trades Chem.*, **18**, 424 (1934); *Chem. Abs.*, **28**, 6340 (1934).

[13] Deforge, A., *Halle aux cuirs*, 36, 83 (1928); Grasse, G., *Cuir tech.*, **20**, 141 (1931).

[14] Cuccudoro, M., *Boll. ufficiale staz. sper. ind. pelli mat. concianti*, **10**, 237 (1932); *Chem. Abs.*, **27**, 624 (1933).

[15] Further reviews of these methods have been given by Desmurs, G., *Cuir tech.*, **21**, 40, 57, 77 (1932); Karsten, A., *Ledertech. Rundschau*, **26**, 93 (1934); *Cuir tech.*, **23**, 330 (1934); **24**, 36 (1935); **24**, 198 (1935). Karsten described a fluorescence microscope for use in the leather industry.

[16] de la Bruère, A., *J. Soc. Leather Trades Chem.*, **9**, 427 (1925); *Chem. Abs.*, **19**, 3384 (1925); Deforge, A., *Halle aux Cuirs*, 131 (1929).

[17] Theis, E. R., and Serfass, E. J., *J. Am. Leather Chem. Assoc.*, **33**, 67 (1938).

[18] Vlès, F., and Gex, M., *Compt. rend.*, **180**, 140 (1925).

[19] Vellinger, E., and Klinkenberg, A., *Ann. combustibles liquides*, **10**, 79 (1935); *Chem. Abs.*, **29**, 3815 (1935).

[20] Luszczak, A., *Abhandl. Gesamtgebiete Hyg. No.* **22**, 59 (1926); *Chem. Abs.*, **31**, 4801 (1937). Certain photochemical reactions of Russian petroleum have been discussed by Pyhälä, E., *Mat. grasses*, **23**, 9124, 9182 (1931).

[21] Schou, S. A., and Bendix-Nielsen, I. B., *Dansk Tidskr. Farm.*, **4**, 1 (1930); *Brit. Chem. Abs.*, **B**, 263 (1930); *Arch. Pharm.*, **272**, 761 (1934); *Chem. Abs.*, **29**, 915 (1935).

[22] Vellinger, E., and Marchand, P., *Ann. combustibles liquides*, **5**, 977 (1930); *Chem. Abs.*, **25**, 4391 (1931); Vellinger, E., *Ann. combustibles liquides*, **12**, 195, 250 (1937); *Chem. Abs.*, **31**, 7629 (1937).

With air, the change in color is not as distinctive, but insoluble oxidation products are formed. Shile and Avakova [23] find paraffin containing more than 0.1 per cent of oil to be unstable toward ultraviolet rays. Such paraffin, treated with fullers' earth and exposed to ultraviolet rays, is light-stable.

Heavy liquid pharmaceutical petrolatums of different geographical origins differ considerably in resistance to spoiling by exposure to sunlight in flint glass bottles.[24] The light-stability can be measured by comparatively short exposures of the oil in flint bottles to ultraviolet light.

It was once suggested that ultraviolet light be employed in the cracking of petroleum oils. They were to be heated with a catalyst and sprayed through an irradiated zone.[25] A patent to Physical Chemistry Research Co.[26] described the preparation of liquid hydrocarbons suitable for use as fuels by distilling solid fuels and subjecting the resulting gases, together with carbon monoxide and hydrogen, to the action of both ultraviolet rays and a high-potential electrostatic field.

Egloff [27] heats normally incombustible hydrocarbon gases from oil-cracking under superatmospheric pressure to about 650 to 1000°C., then lowers the pressure on the gases and subjects them to the action of ultraviolet light..[28]

Miller [29] renders solar light petroleum distillates, refined by treatment with silica gel, sweet to the "doctor test" by exposure to the radiations from a mercury-vapor lamp. Morrell [30] treats hydrocarbon distillates containing mercaptans by converting them to mercaptides by treatment with "Sunlite" solutions and then precipitates the mercaptides by exposing the products to ultraviolet light.

The bloom or fluorescence of petroleum oil may be destroyed by ultraviolet rays.[31] Some oils are thereby reddened in color or otherwise slightly darkened. Other oils are bleached by such treatment. Petroleum oils intended for use as lubricants and which may have gumming properties due to unsaturated components are improved in quality by exposure to ultraviolet rays in an inert gas. Apparently polymerization occurs, resulting in the formation of saturated bodies. Gray [32] deblooms lubricating oil, paraffin wax and the like and brings about partial conversion to acids and esters by blowing air through the hydrocarbon material at 50 to 120°C., while exposing it to ultraviolet rays. Catalysts may be present and the operation may take place at pressures up to five atmospheres. Gray states that he has been able to convert 75 per cent of the hydrocarbon material into fatty acids by this process.

Color Changes. Gasolines refined from certain California crude oils not treated by clay or acid tend to take on a color which may be pink, yellow or light chocolate when the product is dispensed in a visible pump in the presence of sunlight. McConnell [33] proposed to treat such oils by exposing them to daylight for

[23] Shile, V. N., and Avakova, E. S., *Nestyanoe Khozyaistvo,* **25,** No. 9, 59 (1933); *Chem. Abs.,* **28,** 4886 (1934).

[24] Green, L. W., and Schoetzow, R. E., *J. Am. Pharm. Assoc.,* **21,** 1286 (1932); *Chem. Abs.,* **27,** 1987 (1933).

[25] French P. 469,948, 1914, to Continental Caoutchouc and Gutta-Percha Co.

[26] British P. 357,206, June 4, 1929, to Physical Chemistry Research Co.; *Chem. Abs.,* **26,** 4701 (1932).

[27] Egloff, G., U. S. P. 1,904,362, April 18, 1933; *Brit. Chem. Abs.,* **B,** 134 (1934).

[28] For a patent relating to the utilization of ultraviolet rays for supporting combustion in heat engines, see Gill, H. A., British P. 269, 808, Nov. 9, 1926.

[29] Miller, E. B., U. S. P. 1,647,459, Nov. 1, 1928; *Chem. Abs.,* **22,** 315 (1928).

[30] Morrell, J. C., U. S. P. 1,904,382, April 18, 1933, to Universal Oil Products Co.; *Chem. Abs.,* **27,** 3601 (1933).

[31] Ellis, Carleton, U. S. P. 1,089,359, March 3, 1914.

[32] Gray, T. T., U. S. P. 1,158,205, Oct. 26, 1915.

[33] McConnell, J. R., U. S. P., 1,590,841; June 29, 1926; *Chem. Abs.,* **20,** 3077 (1926).

fifteen to thirty or more daylight hours to fix the color or complete the color reaction to its maximum and then remove the discoloring compound, preferably by distillation. In this process, the sensitive portion, which is probably an organic sulfur compound, is rendered non-volatile and remains in the residue on distillation. The distillate then retains its freedom from color on exposure to sunlight. The process is known as complete fixation. It is said that the process may also be applied to the first pressure distillate of cracked gasoline and so obviate the necessity of treating a large percentage of the cracked gasoline with either acid or clay.

Even paraffin has been improved in its fastness to light by treating it with decolorizing agents and radiations of short wave-lengths together or in turn. Oxygen may be supplied during the irradiation.[34]

Kovalev and Illarionov [35] exposed Grozny petroleum distillates to sunlight for three months with free access of air. Kerosene, light and heavy solar oil, spindle oil, engine oil and cylinder oil were used. The specific gravity and refractive indices of the samples changed very little. The dielectric constant increased at first, but after two months decreased. The drop in the third month is explained by supposing that rearrangement takes place in an oxygen compound, the added active oxygen being given to other unsaturated molecules forming ketoxy and oxy-compounds. No aldehydes were found. Panchenkov and Puzitsckiĭ,[36] however, state that certain wave-lengths increase the viscosity of lubricating oils.

In testing the color stability of gasoline to sunlight, Hoeman [37] used a ferric oxalate actinometer for gauging the intensity of the sunlight at the time the test exposures on the gasoline are made. Lowry, Smith and Murphy [38] standardized a carbon arc source against the summer sun in testing the color change in gasolines. The samples were exposed in 4-oz. oil bottles of ordinary glass, Corex glass and quartz. It was found that a West Texas gasoline, when exposed in glass to a cerium-containing carbon arc, changed in color from Saybolt 22° to 17° in ten minutes. Another listed as "commercial gasoline B" changed from 23° to 17° in thirty minutes.

A study of the way in which some gasolines become hazy and discolored and deposit sediment in a glass dispensing bowl has been made by Morrell, Benedict and Egloff.[39] In reviewing earlier work,[40] they state that it had been indicated that color formation in gasolines is due to oxidation reactions involving sulfur compounds or unsaturated hydrocarbons. Samples of Midcontinent straight-run gasolines, cracked gasoline and a blend of equal parts of straight-run and cracked gasoline were exposed in quartz cylinders for an hour to a carbon arc in the presence of air, oxygen, nitrogen, carbon dioxide or hydrogen. In the presence of air or oxygen, all samples developed color, gum, peroxides, acids and aldehydes. Although the straight-run and blended gasolines developed haze, the cracked ones did not. Cracked and blended gasolines developed more gum in oxygen than did

[34] German P. 475,343, Aug. 28, 1926, to Werschen-Weisserfelser Braunkohlen, A. G.; *Chem. Abs.,* **23,** 3341 (1929). See also[22].

[35] Kovalev, T. G., and Illarionov, V. V., *J. prakt. Chem.,* **138,** 306 (1933); *Chem. Abs.,* **28,** 1513 (1934).

[36] Panchenkov, G. M., and Puzitsckiĭ, K. W., *J. Gen. Chem. (U.S.S.R.),* **7,** 394 (1937); *Chem. Abs.,* **31,** 4800 (1937).

[37] Hoeman, E. C., *Oil and Gas J.,* **32,** No. 17, 18 (1933); *Chem. Abs.,* **27,** 5525 (1933).

[38] Lowry, C. D., Jr., Smith, M. A., and Murphy, G. B., *Ind. Eng. Chem. (Anal. Ed.),* **7,** 140 (1935).

[39] Morrell, J. C., Benedict, W. L., and Egloff, G., *Ind. Eng. Chem.,* **28,** 122 (1936); Egloff, G., Morrell, J. C., Benedict, W. L., and Wirth, C., *Ind. Eng. Chem.,* **27,** 323 (1935).

[40] Brooks, B. T., *Ind. Eng. Chem.,* **18,** 1203 (1926); Brooks, B. T., and Parker, H. O., *Petroleum,* July 14, 1924; Carpenter, J. A., *J. Inst. Petroleum Tech.,* **12,** 518 (1926); *Chem. Abs.,* **21,** 1702 (1927).

straight-run gasolines. Under inert gases, the straight-run gasoline dropped in color from 30° to 28° only, and the cracked and blended gasolines were unaffected. There was no formation of acid or gums and only very small amounts of peroxides.

The addition of sulfur (0.01 to 0.1 per cent) was deleterious either in the presence or absence of oxygen. With air or oxygen, it caused a marked increase in the amounts of color and gum formed. The acid formation and peroxide number were also greater than in the absence of added sulfur. With added sulfur, the color depreciation and gum formation were less in the absence of oxygen, no haze or acids appearing and only very small amounts of peroxides developing. Hydrogen sulfide was evolved in all cases. Oxygen is necessary for the formation of haze, acids or peroxides, but not always for the formation of gum or color. The elemental sulfur was almost completely removed as such during exposures either with or without oxygen. Oxides of sulfur were formed.

The addition of *n*-propyl disulfide (representative of disulfides likely to be present in gasolines or formed by sweetening) decreased the color stabilities in light and air of straight-run and blended gasolines. The decreases were greater in oxygen and even the cracked gasoline was affected. The disulfide had, however, no effect on the gum formation in gasolines exposed to air, although in those exposed to oxygen it caused a small increase. The peroxide number of the straight-run gasoline was lower and the acid number higher than in the absence of added disulfide. This was not, however, true of the cracked gasoline. Disulfide addition caused no depreciation of gasolines exposed in hydrogen, nitrogen or carbon dioxide. Mercaptans were formed during exposures in non-oxidizing atmospheres.

No fixed relation was found between color and gum formation. They can form simultaneously or gum can form with no color depreciation; or color can form without an increase in the gum content. Haze particles contain sulfur dioxide and trioxide or the corresponding acids and organic material. Most of the acid formed in gasoline was found in the haze particles which could be removed by filtration through filter paper. Although this improved the color, it did not affect the gum content of the gasoline.

Results obtained with Pennsylvania and California gasolines were similar, with the following exceptions. The Pennsylvania straight-run gasolines with no added sulfur compounds did not form gum on exposure to light and air, although gum was formed in oxygen. The addition of *n*-propyl disulfide caused slight increases in gum formation in the Pennsylvania cracked gasoline and in all of the California gasolines. The results with the inert atmospheres were the same as with the Mid-continent gasolines.

These workers have again recently emphasized that color is formed only in the presence of sulfur or *n*-propyl disulfide.[41]

Pure hydrocarbons exposed to the carbon arc under oxygen give traces of peroxides, acids and aldehydes. The bromine number and refractive index are unchanged by light, either in the presence or absence of sulfur and propyl disulfid.[42]

Vellinger and Radulesco[43] exposed samples of motor fuels under oxygen in closed Pyrex containers to the rays of a mercury lamp and found the amount of gummy material formed to be a function of the rate of absorption of oxygen. At the beginning, the quantity of gum formed was almost proportional to the amount of oxygen absorbed. Gradually, however, the absorption of oxygen diminished

[41] Morrell, J. C., Benedict, W. L., and Egloff, G., *Ind. Eng. Chem.*, **28**, 122, 448 (1936).

[42] Note also Berger, G. W., *Refiner Natural Gasoline Mfr.*, **15**, 411 (1936).

[43] Vellinger, E., and Radulesco, G., *Compt. rend.*, **196**, 1495 (1933); *Ann. combustibles liquides*, **8**, 883 (1933); *Chem. Abs.*, **28**, 621 (1934).

and approached a limit set by the particular pretreatment to which the sample had been subjected.

On the other hand, Freund[44] believed the absorption of oxygen of secondary importance. He considered the resins to be formed from complicated unsaturated hydrocarbons. A brief irradiation resinified only the most unstable unsaturated compounds. The resinous, gum-forming compounds produced in petroleum-cracked products by ultraviolet rays increased in amount with the exposure. Extremely small amounts were formed in comparison in primary benzines, paraffins, naphthenes and aromatic and simple unsaturated hydrocarbons. It was found that sulfur and oxygen compounds were almost completely removed from the benzines during separation of the resin.[45]

The larger the storage tank, the slower the diffusion of oxygen and the less the gum formation. Sunlight lowers the induction period for gum formation, but water has the opposite effect. The rate of gum formation roughly triples for every twenty degrees rise in temperature.[46]

To stabilize cracked distillates, especially from California or asphaltic base crudes, which contain more unsaturated and unstable constituents and more gum and coloring matter than the straight-run distillates from the same sources, Davis[47] employed a photochemical reaction. Daylight, sunlight or artificial ultraviolet sources were used and the undesirable constituents were oxidized in the presence of copper oxide. They formed organic acids which produced copper salts soluble in the oil and removed from it by subsequent distillation. A continuous stream of hydrocarbons in the vapor state mixed with oxygen can also be conveyed past a source of ultraviolet light and the oxidized products condensed, according to Martin.[48]

Tauss[49] proposed to remove the resin-forming constituents in the refining of hydrocarbon oils by accelerating their polymerization by treating the hot oil or its vapor with very small amounts of oxygen and then removing the polymerization products. Other means could be used also, such as a glow discharge, irradiation or the addition of small amounts of acid or alkalies.

By a similar method, Goltstein[50] polymerized constituents in petroleum and similar hydrocarbons, thereby changing the physical characteristics of the distillate. By using an immersed quartz mercury-vapor lamp, at 60 volts and 6 amperes, the viscosity (Engler) of Russian mineral oil was increased from 6.4 to 7.8 in a half hour. The treatment may be applied to either the liquid or to the vapor phase during distillation.

In the cracking and distillation patent of Tingley,[51] the oil is subjected to the action of emanations from a radioactive substance or to ultraviolet rays before it enters a conduit within the furnace of the apparatus.

Light-stability may also be increased in cracked gasoline by the addition of 0.01 to 0.5 per cent of triacetoxytriethanolamine or other esters of the general formula $(RCOOR')_nNH_x$ in which R′ is aliphatic, R aliphatic or aromatic, x is 0, 1 or 2 and n 1, 2 or 3.[52]

Testing of Gasolines. The stability of gasolines may be tested by ultraviolet light in order to predict the tendency of the samples to form gums. Allusion

[44] Freund, M., *Brenzstoff-Chem.*, **14**, 61 (1933); *Chem. Abs.*, **27**, 3808 (1933).

[45] Freund, M., see also *Proc. World's Petroleum Congress*, **2**, 108 (1933); *J. Inst. Petroleum Tech.*, 83A, (1934); Balada, A., *Petroleum Z.*, **31**, No. 48, 11 (1933).

[46] McNamara, T. L., *Refiner and Natural Gasoline Mfgr.*, **13**, 381; *Chem. Abs.*, **29**, 2721 (1935).

[47] Davis, R. F., U. S. P. 1,551,806, Sept. 1, 1925.

[48] Martin, R. B., U. S. P. 1,678,403, July 24, 1928, to Mineral Separations N. Am. Corp.; *Brit. Chem. Abs.*, **B**, 702 (1928).

[49] Tauss, J., German P. 475,277, Dec. 1, 1923; *Chem. Abs.*, **23**, 3340 (1929).

[50] Goltstein, E., British P. 249,895, Sept. 30, 1924; *Chem. Abs.*, **21**, 1007 (1927).

[51] Tingley, S. L., U. S. P. 1,627,937-8, May 19, 1927; *Brit. Chem. Abs.*, **B**, 516 (1927).

[52] Mikeska, L. A., and Holtzclaw, J. B., U. S. P. 2,110,274, March 8, 1938; *Chem. Abs.*, **32**, 3600 (1938).

to this appeared in a patent of Somerville and Hoffert.[53] Some have stated that the action of ultraviolet light is too severe as it resinifies certain compounds which remain stable on prolonged storage.[54] As a result the conclusions of such accelerated tests are not always in agreement with those obtained after storage for nine months. Nevertheless, the method has been frequently proposed. Beard and Reiff [55] standardize the radiations employed by their effect on an oxalic acid-uranyl acetate actinometer, and consider the effects of temperature. They note that discoloration started under radiation increases in darkness, which suggests a chain process. Schulze and Frey [56] exposed the fuel to actinic light rays while treating it with an aqueous solution of glycol and water as a separate liquid phase.

Woog, Givaudon and Dacheux [57] found that the use of white light in tests for potential gum gave unsatisfactory results. The effect of ultraviolet light was determined by exposing the sample, first in crystallizing dishes covered with Cellophane and later in Pyrex glass to a quartz mercury arc (5.4 amp., 110 volts) at about 30 cm. The results were very decisive and revealed a difference in the quality of two gasolines between which bomb tests had failed to show a difference. The tests were completed by bomb tests following the irradiation. Sufficiently reproducible results could be obtained when the gum did not exceed 10 mg. For higher values, the accuracy dropped to 10 per cent. The optimum conditions were thought to be ultraviolet treatment for one hour and heating at 100°C. for three hours. For ordinary gasoline, ultraviolet treatment for thirty minutes and heating for two hours sufficed.

Freund [58] found the results obtained by ten minutes of ultraviolet irradiation agreed closely with those of storage tests. The elementary composition of the gum so formed appeared to be the same as that formed during storage in darkness or under the influence of oxygen.

Baxter [59] observed gum formation in samples of gasoline derived from Colorado shale oil when treated in the presence of oxygen with sunlight, ultraviolet light or x-rays. Birch and Stansfield [60] found that samples of cyclohexane gave 0.2 gm. of peroxide oxygen per liter in a sample kept in light for six months and only 0.009 gm. per liter in a sample kept in darkness. No visible gum, however, deposited in the light sample. Cyclohexane in contact with air shows indications of the presence of peroxides after a short exposure to ultraviolet light.

In a patent of Rosenstein and Hund [61] on the addition of selenomercaptan to produce antiknocking gasolines, it was stated that untreated gasolines containing 62.2 mg. of gum per 100 cc. had after exposure to ultraviolet light for 24 hours a gum content of 102.9 mg. per 100 cc.. Selenomercaptan-treated samples had 33.5 mg. per 100 cc. before and 33.7 mg. after a similar irradiation. It was believed that this treatment with selenomercaptan checks the tendency to gum formation and may render unnecessary any previous fixation process for the removal of unsaturated materials.

[53] Somerville, P. G., and Hoffert, W. H., British P. 289,347, Oct. 27, 1926; *Chem. Abs.*, **23**, 689 (1929).

[54] Brunschwig, R., *Chal. et ind.*, 315, Oct., 1928; *Brit. Chem. Abs.*, **1929B**, 931; Brunschwig, R., and Jacqué, L., *Compt. rend.*, **189**, 486 (1929).

[55] Beard, L. C., Jr., and Reiff, O. M., *Ind. Eng. Chem. (Anal. Ed.)*, **3**, 280 (1931).

[56] Schulze, W. A., and Frey, F. E., U. S. P. 1,950,697, March 12, 1934, to Philips Petroleum Co.; *Chem. Abs.*, **28**, 3562 (1934).

[57] Woog, P., Givaudon, J., and Dacheux, P., *Rev. petrolifere, No.* **584**, 721 (1934); *Chem. Abs.*, **28**, 7502 (1934).

[58] Freund, M., *World Petroleum Congress, London, Proc.* **2**, 108 (1933); *Chem. Abs.*, **28**, 4879 (1934).

[59] Baxter, R. A., *Ind. Eng. Chem.*, **21**, 1096 (1929).

[60] Birch, S. F., and Stansfield, R., *Nature*, **123**, 490 (1929).

[61] Rosenstein, L., and Hund, W. J., U. S. P. 1,835,184, Dec. 8, 1931.

Lead tetraethyl in gasolines may be stabilized against light and water by a small amount of a water-soluble fluoride.[62] One of the drawbacks to the use of iron pentacarbonyl as an antiknock agent is its instability to sunlight. Irlin and Solodovnik [63] propose the use of dyes as stabilizers to avoid this.

Other Applications to Petroleum Products. Chlorinated hydrocarbons for dry-cleaning, such as perchloroethylene, trichloroethylene and tetrachloroethylene, may be made stable to light by the addition of small amounts of butyl oxide, chloride or tartrate, Tetralin or Decalin.[64] Mitscherling [65] claims the formation from gasoline of alcohols and ketones by the action of a rare-gas lamp, such as one containing argon or neon. The irradiation is conducted in the presence of an oxidizing agent, such as a perborate or percarbonate, and a metal compound, such as copper hydroxide, to increase the electrical conductivity of the hydrocarbon material.

Irradiation with violet or ultraviolet light, x-rays, cathode rays, etc. has been suggested by Herbsman [66] for the separation of the components of such dispersed systems as petroleum-water emulsions or foams.

Drugs and Related Products

There have been a few who have claimed to increase the potency of drugs by the application of ultraviolet rays. Cunningham and Macbeth [67] add fluorescent substances, such as quinine sulfate, to the liquid under treatment, vaporize it through an atomizing nozzle, and subject the vapor to the action of ultraviolet rays. Abrahamowicz [68] has proposed to treat arnica, camomile, pine needles, coltsfoot, lime or elder blossoms or stinging nettles, while dry, with both x-rays and ultraviolet rays, before using them in cataplasms.

Such claims are not well substantiated. No widely used applications are known, other than to the production of vitamin D discussed in a subsequent chapter.

Instead, pharmacists have long realized that light, and particularly, the shorter wave-lengths, exerts a deleterious action upon many drug preparations. Elaborate studies, too detailed for inclusion here, on the extent to which this may occur have been conducted by Arny, Taub and Steinberg.[69] Their work was mainly directed to spectrophotometric determinations of the transmissions of various wave-lengths by the types of containers available on the American market. In general, from three to twelve times as much deterioration occurred in direct light as compared with diffused light. About 15 per cent of the drugs and chemicals tested were light-sensitive. Amber glass gave the best protection from ultraviolet rays. Red-flashed glass and Corning Red were very effective but are expensive. Few reputed stabilizers gave satisfactory results, although tin compounds stabilized phenol and, as is well known, acetanilide stabilizes hydrogen peroxide.

[62] Michel, J. M., U. S. P. 2,067,331, to I. G. Farbenind. A.-G.; *Chem. Abs.*, **31**, 1603 (1937).

[63] Irlin, A. L., and Solodovnik, *Novosti Tekhniki, No. 26*, 20 (1936); *Chem. Abs.*, **31**, 2404 (1937).

[64] de Schacken, J. M. G., and Schmidt, M. E. A., French P. 794,878, Feb. 27, 1936; *Chem. Abs.*, **30**, 5430 (1936).

[65] Mitscherling, W. O., U. S. P. 2,003,303, June 4, 1935; 2,003,898; *Chem. Abs.*, **29**, 4771, 4931 (1935).

[66] Herbsman, A. M., British P. 356,926, Aug. 27, 1930; U. S. P. 1,783,471; *Chem. Abs.*, **25**, 365 (1931).

[67] Cunningham, E. L., and Macbeth, H. F., U. S. P. 1,659,085, Feb. 14, 1928; *Chem. Abs.*, **22**, 1440 (1928).

[68] Abrahamowicz, J., British P. 455,914, 1936; *Chem. Abs.*, **31**, 2359 (1937).

[69] Arny, H. V., Taub, A., and Steinberg, A., *J. Am. Pharm. Assoc.*, **20**, 1014, 1153 (1931); *Chem. Abs.*, **26**, 1395 (1932); Arny, H. V., *Glass Packer*, **12**, 497 (1933); *Chem. Abs.*, **27**, 5913 (1933); Brunner, K., *Pharm. Zentralhalle*, **77**, 696, 721, 756, 783 (1936); Husa, W. J., *Glass Container*, **7**, No. 12, 9 (1928); *Chem. Abs.*, **23**, 236 (1929).

Eisenbrand [70] believes that for highly sensitive substances, violet manganese glass is best. For less sensitive drugs, brown iron glass will usually suffice.

Rojahn [71] gave data on a number of alkaloidal solutions and tinctures. An exposure of a year to sunlight reduced the strength of tincture of hydrastis about 25 per cent and of tincture of capsicum 35 per cent. The tinctures of aconite, areca, belladonna, granatum and strophanthus were relatively stable, the losses being under 5 per cent. Alkaloidal and alkaloidal salt solutions, after 24 hours irradiation by ultraviolet light, suffered losses up to 31.3 per cent (cinchonidine). Cocaine was least affected. The losses were 23.6 per cent in tincture of hydrastis, 35.1 per cent in tincture of capsicum and 28 per cent in tincture of areca. The optical rotation also was lessened. The color of tincture of capsicum was decreased by exposure to daylight. In the tinctures of granatum, hydrastis and areca, it was increased.

Tribromoethyl alcohol is very unstable in light.[72] An exception to the behavior of many pharmaceutical preparations is offered by the decolorized solution of iodine which, according to Merry,[73] should be kept in colorless glass containers exposed to sunlight.

The mydriatic action of homatropine hydrobromide is not decreased by exposure to ultraviolet light, according to Pittenger and Krantz.[74] On the other hand, Macht and Krantz,[75] found that ultraviolet rays produce a rapid deterioration of the tincture of digitalis.On prolonged exposure, a point is reached at which there are formed products of increased toxicity for both plants and animals. On further exposure, a secondary weakening in potency occurs. Ultraviolet and polarized visible light were said also to cause a decrease in the anesthetic action of some isomeric octyl alcohols.[76] Macht and Hill [77] were unable to detect any loss of the antiseptic or germicidal action of 1 : 500 solutions of Mercurochrome-220 after exposure to ultraviolet rays or to polarized visible light. Krantz and Carr [78] found that elixir of pepsin and rennin became less acid on irradiation, but samples stored in amber glass compared favorably after six weeks in direct light (supplemented by Alpine lamp irradiation for one-half hour each week) with fresh preparations.

The toxicity of quinine for infusoria is increased by ultraviolet irradiation of its solutions, provided the intensity is sufficient. If too great, however, the fluorescense is increased and the toxicity decreased.[79]

It has been noted [80] that finely ground pyrethrum powders lose most of their toxicity in a few days of exposure to summer sunlight and air. With finely ground derris, the loss was about half as rapid. A one-hour exposure to a mercury-vapor lamp was equal in detoxicating power to eight hours of July sunlight and was

[70] Eisenbrand, J., *Pharm. Ztg.*, **72**, 1275 (1927); **74**, 263 (1929); *Chem. Abs.*, **22**, 137 (1928); **23**, 2247 (1929).

[71] Rojahn, C. A., and Herzog, H., *Pharm. Zentralh.*, **73**, 401 (1932); *Chem. Abs.*, **26**, 5173 (1932); Rojahn, C. A., and Haase, E., *Pharm. Zentralh.*, **74**, 625 (1933); *Chem. Abs.*, **28**, 855 (1934).

[72] Fialkov, Y. A., *Farm. Zhur., No.* **3**, 184 (1937); *Chem. Abs.*, **32**, 3905 (1938).

[73] Merry, J. J. F., *Pharm. J.*, **140**, 347 (1938); *Chem. Abs.*, **32**, 3909 (1938).

[74] Pittenger, P. S., and Krantz, J. C., Jr., *J. Am. Pharm. Assoc.*, **17**, 1081 (1928); *Chem. Abs.*, **23**, 1214 (1929).

[75] Macht, D. I., and Krantz, J. C., Jr., *Proc. Soc. Exptl. Biol. Med.*, **23**, 340 (1926); Macht, D. I., *Arch. Phys. Therapy, X-ray, Radium*, **13**, 5 (1932); *Chem. Abs.*, **26**, 1667 (1932).

[76] Schroeder, H., and Macht, D. I., *Arch. exptl. Path. Pharmakol.*, **158**, 53 (1930); *Chem. Abs.*, **25**, 4049 (1931).

[77] Macht, D. I., and Hill, J. H., *J. Am. Pharm. Assoc.*, **16**, 110 (1927).

[78] Krantz, J. C., Jr., and Carr, C. J., *J. Am. Pharm. Assoc.*, **19**, 32 (1930).

[79] Fedorov, B. T., *Bull. soc. naturalistes Moscou, Sect. biol.*, **44**, 119 (1935); *Chem. Abs.*, **30**, 2643 (1936).

[80] Badertscher, A. E., and Wotherspoon, R., *Soap (Sanitary Products Section)*, **11**, No. 4; **87**, 111, 113 (1935); *Chem. Abs.*, **29**, 4125 (1935).

more constant and easily controlled. Extracts in petroleum distillates were exposed by Hoyer [81] in tight flint-glass bottles to sunlight and daylight for four months and at intervals tested for their toxic action on flies. Sprays prepared with an odorless base gained slightly in toxicity during the first four days, but a sample prepared in an ordinary petroleum distillate lost toxicity from the start. After the fourth day, all samples lost toxicity rapidly, the loss being 65 per cent at two months and 90 per cent at four months. The increase observed in some at the start may have been due to the formation of an unstable toxic substance. The sprays with odorless base became hazy within three hours and their amber color was gradually lost. Finally, a white precipitate settled out. The sample with the ordinary base remained clear but lost some of its color. Chemical assays did not give consistent results. Pearson [82] found that the substitution of some of the pyrethrum by pine oil retards some of the changes.

Fleming and Baker [83] found that exposure to ultraviolet light reduces the value of rotenone as a stomach poison for the Japanese beetle, although the value of derris and rotenone as repellants was but slightly reduced by exposure for 24 hours.

Prolonged sun-drying of pyrethrum caused appreciable losses, but quick drying in the sun did not.[84] According to Jones, Gersdorff, Gooden, Campbell and Sullivan,[85] the photochemical decomposition of dry rotenone does not take place in the absence of oxygen. Rotenone, its hydrochloride, rotenone-bentonite mixture, derris root and derris extract lost more than half their toxicity during a ten-day exposure to sunlight. Arc light practically destroyed their toxicity. Dihydrorotenone was more resistant, requiring twenty days in sunlight, but in arc light it lost toxicity to about the same extent as rotenone. Lampblack afforded some protection.

Anthelmintic capsules of tetrachloroethylene intended for animals, may be stabilized against light [86] by incorporating an oil-soluble red dye such as Oil Soluble Red O. Deichsel [87] uses 0.5 per cent of the azo- dye from *o*-anisidine and β-naphthol to make light-stable a solution comprising a terpene oxide such as ascaridol.

Tobacco. Ultraviolet light is occasionally applied to tobacco for the purpose of killing molds on the leaves. It has also been recommended for slightly altering the color. Dorcas [88] states that this may have important applications in foreign markets, but in the United States is not particularly important, except for leaves intended to serve as cigar wrappers. Exposure to ultraviolet also causes a number of little understood changes in the quality of the tobacco.

The Neuerburg'sche Verwaltungs Gesellschaft [89] claimed that the denicotinizing of tobacco by fermentation may be accelerated by irradiation with wave-lengths shorter than 4000A and that the application of ultraviolet light improves tobacco which has been tainted and partly degraded by mold and other micro-organisms. Richter [90] claimed to reduce the toxicity of cut or sliced tobacco by exposing it on an endless conveyor belt to

[81] Hoyer, D. G., *Soap (Sanitary Products Section)*, **11**, No. 12, 105, 107, 109, 111 (1935); *Chem. Abs.*, **30**, 786 (1936).

[82] Pearson, A. M., *Del. Agr. Expt. Sta. Bull.*, **196**, 5 (1935); *Chem. Abs.*, **30**, 3570 (1936).

[83] Fleming, W. E., and Baker, F. E., *J. Agr. Research*, **53**, 197 (1936); *Chem. Abs.*, **30**, 8497 (1936).

[84] Beckley, V. A., and McNaughton, F., *E. African Agr. J.*, **2**, 327 (1937); *Chem. Abs.*, **31**, 5503 (1937).

[85] Jones, H. A., Gersdorff, W. A., Gooden, E. L., Campbell, F. L., and Sullivan, W. N., *J. Econ. Entomol.*, **26**, 451 (1933); *Chem. Abs.*, **27**, 4015 (1933).

[86] Anderson, C. N., U. S. P. 1,703,377, Feb. 26, 1929, to Parke Davis and Co.; *Brit. Chem. Abs.*, B, 453 (1929).

[87] Deichsel, S., U. S. P. 2,066,717, to Winthrop Chemical Co.; *Chem. Abs.*, **31**, 1040 (1937).

[88] Dorcas, M. J., *Trans. Illum. Eng. Soc.*, **28**, No. 7, 575 (1933).

[89] German P. 507,194 and 527,361, 1928, to Neuerburg'sche Verwaltungs Gesellschaft; *Chem. Abs.*, **25**, 560, 4664 (1931). See, however, Chapter 27.

[90] Richter, C. M., British P. 359,920, May 3, 1929; *Chem. Abs.*, **26**, 4916 (1932).

ultraviolet, infrared or visible light of specified wave-lengths. Pacini [91] first dampened the tobacco with water containing a "sauce" which may contain coumarin, etc. and an agent such as glycerol, ethylene glycol, malic, or tartaric acid which was believed to counteract the opacity of the other constituents of the sauce, before irradiating it.

Lilienfield [92] claimed the irradiation would render mild and cure, strong, previously aged and fermented tobacco leaves.

Chesley [93] subjects cured and aged tobacco to ultraviolet rays which constitute a selected portion of the light used. It is applied by special carbon arc lamps, the tobacco being continuously moved in a revolving drum to subject every part to the action of the rays without appreciably reducing the moisture content. There also was used a small proportion of infrared and visible radiation. Wix and Bunker [94] treat tobacco in a drum, part of the wall of which is of quartz, by a mercury arc.

In a curious method of preserving the aroma of tobacco, Senftner [95] incloses it in an envelope of cellulose material the pores of which are filled with ergosterol or cholesterol which may be irradiated.

Although the discussion (Chapter 27) of the irradiation of nicotine would indicate that the alkaloid cannot be destroyed in tobacco leaves by irradiation for a reasonable time, it has been claimed that the alkaloids in tobacco, tea, coffee, etc. may be decomposed by irradiating the products in the presence of a 1.5-per cent sodium bicarbonate solution.[96]

Alcoholic Beverages. According to Henri, Helbronner and von Recklinghausen [97] wines may be quickly aged by ultraviolet irradiation. According to Petri,[98] exposure of wine to ultraviolet radiation for 0.6 to 4 seconds had no effect on the rate of fermentation, on the production of acids during maturation, or on the vitamin D content, but there may have been an insignificant increase in the content of vitamin C.

From time to time, it has been proposed to age whisky by ultraviolet light, but little or no application seems to have been made of such processes. Mancini and Archangel [99] would pass the rays into the whisky through quartz rods. The use of ultraviolet or infrared rays or a high-frequency or high-tension current in the aging of liquors is suggested by Stein.[100] Merory [101] irradiates the vapors during distillation.[102] Philipsky [103] ages mead by irradiation. The non-aromatic constituents are removed and only the bouquet-producing extract is irradiated.

[91] Pacini, A. J., U. S. P. 1,920,588, Aug. 1, 1933; *Chem. Abs.*, **27**, 4882 (1933).

[92] Lilienfield, W. E., U. S. P. 1,731,018, 1929; *Chem. Abs.*, **23**, 5547 (1929).

[93] Chesley, A. L., U. S. P. 1,926,035, 1933, to American Tobacco Co.; *Chem. Abs.*, **27**, 5898 (1933); British P. 349,174, Feb. 21, 1930.

[94] Wix, A., and Bunker, S. W., British P. 421,487, Dec. 21, 1934; *Chem. Abs.*, **29**, 3786 (1935).

[95] Senftner, G., U. S. P. 1,920,483, 1933; *Chem. Abs.*, **27**, 4882 (1933).

[96] Popoff, M., German P. 565,373, July 6, 1929; Kennedy, D. J., U. S. P. 1,859,740, May 24, 1932; *Chem. Abs.*, **26**, 3857 (1932).

[97] Henri, V., Helbronner, A., and von Recklinghausen, M., U. S. P. 1,130,400, March 2, 1915.

[98] Petri, W., *Z. unters. Lebensm.*, **64**, 177 (1932); *Chem. Abs.*, **27**, 5469 (1933).

[99] Mancini, J., and Di Archangel, N., U. S. P. 2,040,264, 1936; *Chem. Abs.*, **30**, 4618 (1936); *Brit. Chem. Abs.*, **B**, 487 (1937).

[100] Stein, J.-G., German P. 635,694, Oct. 4, 1936; *Chem. Abs.*, **31**, 805 (1937).

[101] Merory, J., Austrian P. 149,188, April 10, 1937; *Chem. Abs.*, **31**, 5507 (1937).

[102] For the artificial aging of wines by ultraviolet light, note also Lord Investierungs-Korporation, A. G., German P. 638,936, Nov. 25, 1936; 652,858, Nov. 10, 1937; French P. 807,371, Jan. 11, 1937; *Chem. Abs.*, **31**, 3204, 5508 (1937); British P. 468,990, July 16, 1937. A series of sublethal exposures at long intervals is used.

[103] Philipsky, A. J. H., German P. 557,806, March 18, 1933; *Chem. Abs.*, **27**, 559, 4343 (1933).

Miscellaneous Products

That exposure of a polished metal surface to ultraviolet rays may render it increasingly liable to corrosion was indicated by tests conducted at the Bureau of Standards.[104] Specimens of Armco iron, medium carbon steel, stainless steel, and high-nickel steel were used for the test and were irradiated eight hours. Moisture from the breath condensed differently on the exposed and unexposed surfaces, rendering the two easy to distinguish. On the exposed part the drops were larger than on the unexposed part, and the surface looked as if a very thin oil film had been spread over it, making it less easily wetted than the unexposed surface. In the case of medium-carbon steels, very noticeable corrosion of the exposed spots was found to occur after four condensations of moisture, although the rest of the surface was hardly attacked. Chromium and nickel steels did not show any corrosion, although there was the same difference in appearance between the exposed and unexposed surfaces. Jameson [105] has described apparatus for testing the weathering properties of steel plates by exposure to water sprays and ultraviolet rays. Enos [106] believes ultraviolet light increases somewhat the rate of corrosion of various steels. Similar effects are probable with zinc, lead and aluminum.[107] In daylight or artificial light, the rate of corrosion of Electron alloy in sea water decreases with time, although in darkness it remains constant for several days.[108]

Pfeiffer [109] found that the irradiation of 0.5-mm. films of asphalt on clean iron plates leads to the formation of a hard-shrinking skin formed by polymerization and oxidation. Gödrich [110] states that ultraviolet rays render asphalt more insoluble.

Andrews [111] tests road tar by exposing a 1-mm. layer at 150°C. in a given atmosphere to ultraviolet light at 12 inches for twenty hours, with a sheet of Vita glass interposed. After this the penetration of a standard needle, 100 gm. at 5 sec., shall not be less than 50 at the temperature at which the penetration of the original sample was 100.

Neuber and Herberg [112] find that in petroleum asphalts, diffuse sunlight causes a shrinking of the surface layer with the formation of cracks. The oily constituents decrease with the time of exposure. The petroleum resins increase slightly, but the paraffin and ceresin content are hardly changed. The content of hard asphalt increases considerably. The nitrogen content increases considerably, but the sulfur content is unchanged. The carbon content decreases under the short ultraviolet, although it may increase under sunlight.

An accelerated testing cycle involving alternate exposure to a carbon arc and immersion in water has been described by Strieter and Snoke.[113] The wash water is examined for soluble organic products. Acids and ketones are found.

Moisture in the air accelerates the changes in bituminous coatings which occur

[104] *Ind. Eng. Chem.*, **16**, 698 (1924).

[105] Jameson, C. W., British P. 283,539, Jan. 13, 1927.

[106] Enos, G. M., *Ind. Eng. Chem.*, **17**, 793 (1925); see also Bannister, C. O., and Rigby, R., *J. Iron Steel Inst.*, **133**, 293P (1936); Lavenets, I. V., *J. Applied Chem. (U.S.S.R.)*, **10**, 1556 (1937); *Chem. Abs.*, **32**, 2073 (1938).

[107] Bannister, C. O., and Rigby, R., *J. Inst. Metals*, **58**, 227 (1936); *Chem. Abs.*, **30**, 3390 (1936).

[108] Fokeev, V. M., *Vestnik Inzhenerov i Tekh.*, 302 (1933); *Chem. Abs.*, **32**, 5762 (1938).

[109] Pfeiffer, J. P., *Verfkroniek*, **8**, 43 (1935); *Chem. Abs.*, **29**, 4853 (1935).

[110] Gödrich, P., *Monatsh.*, **36**, 535 (1915); *Chem. Abs.*, **9**, 3127 (1915).

[111] Andrews, R. S., *Gas J.*, **205**, 206, 259 (1934); *Chem. Abs.*, **28**, 2162 (1934).

[112] Neuber, F., and Herberg, E., *Mitt. tech. Versuchsamtes*, **24**, 71 (1935); *Chem. Abs.*, **30**, 4658 (1936).

[113] Strieter, O. G., and Snoke, H. R., *J. Research Bureau of Standards*, **16**, 481 (1936); *Chem. Abs.*, **30**, 5326 (1936).

during exposure to 420 hours of variable sunlight. Bituminous coal-tar pitch was less affected than were blown or high-vacuum Mexican asphalt bitumen. In pure oxygen, the benzene-insoluble material of blown Mexican asphalt bitumen increased six times, although the sulfur content suffered but little change.[114]

Ried and Rusleitner[115] find that the activity of natural or artificial fertilizers can be modified by irradiations.

The use of ultraviolet light to ionize air has been suggested as a means of removing static electricity from air in which sprays cannot be avoided.[116] It is also mentioned by Leboucher[117] for preventing the accumulation of charges in the manufacture of linoleum, celluloid, etc. Rathier[118] states that static electricity can be effectively discharged from rolls of paper 750 mm. long and 600 mm. in diameter by exposing the end of the roll for ten minutes at a meter from a mercury arc. This short exposure does not affect the color of the paper. Allingham[119] proposed to make the ionizing of air by ultraviolet light the basis of a method for partially separating the gases.

Kögel[120] in making sound records, uses gelatin and a light-sensitive organic tanning compound. The records are fixed by exposure to light.

Spectrographic Analysis. The applications of spectroscopy in industrial chemistry are so varied and the methods employing the emission spectra of the substances (elements) sought are so intricate that a discussion is not possible in a limited space. It is proving of increasing importance in metallurgy, mining, and in many other fields. A number of books and review articles are available.[121] Of the 27 elements discovered since 1860, fifteen were discovered as a result of optical spectroscopy, four by x-ray spectroscopy, two by their radioactive properties and six by their chemical properties.[122]

Analytical determinations can be made with great accuracy and a few thousandths of a milligram of metals are determinable. However, the accuracies vary from metal to metal and much experience is required for the effective handling of these methods. Histologists have adapted them to the determination of elements in definite portions of tissue sections, *e.g.*, to the determination of calcium in the various coats of the aorta.

Ultraviolet absorption spectra are being more and more widely employed both in analysis and in the study of the constitution of organic compounds. The similarity of many types of absorption spectra is, however, such that the analytical uses of the method are limited. It has been of particular importance in the development of the knowledge of the constitution of vitamins, hormones, and degradation products of chlorophyll and hemoglobin. Illustrative examples of the utility of the method have been given by Fromherz.[123]

Interesting applications have been made of emission spectrography to the study of the flames in an internal combustion engine, particularly when lead tetraethyl and other antiknocking agents are employed.[124]

Fluorescence Analysis. In connection with various topics in the preceding chapters note has been made of the use of fluorescence methods for various analytical determinations. Many other applications of the use of fluorescence in filtered ultraviolet light exist and the method has stimulated a very large number of papers far too great for discussion here. Since no photochemical reactions are necessarily involved, it is unnecessary to devote space to the consideration of the details, particularly since there exist books devoted to the subject.[125] Suffice it to state that the method finds application in the study of documents for age or falsification,[126] It is also used for the detection of fraud in paintings,[127] or of the falsification of water marks in paper,[128] and for other purposes in criminology.[129] It finds varied application in industrial chemistry.[130] For example, the fluorescence of glass may be utilized in control of manufacture and in detection of the age and condition of glass.[131] The so-called "natural" fluorescence has been stated to be dependent upon the physical nature of the glass as well as on its chemical properties. Also, the state of oxidation of the metal or other elements which give fluorescence to the whole was said to be an important factor. In this instance, ultraviolet light may serve as a method of control.

The characteristic fluorescence of glasses has been reported to furnish a method for identification. This was said to be particularly useful in the case of high-priced specialty glasses which sometimes are subject to fraudulent imitation. In some instances there may be introduced into the glass small proportions of substances which would render the glass highly fluorescent in ultraviolet light, without altering the properties and appearance in visible light. It is interesting to note that a fluorescence test may be employed to identify certain of the imitation glasses, such as synthetic resins.[132]

In most of the methods proposed, the ultraviolet light source is used in a dark room in conjunction with a nickel oxide filter which transmits only the region between 3000 and 4000A. Many substances irradiated by these wave-lengths,

[114] Walther, H., *Asphalt Teer Strassenbautech.*, **36**, 1001 (1936); *Chem. Abs.*, **31**, 1597 (1937).

[115] Ried, O., and Rusleitner, K., Austrian P. 136,025, Dec. 27, 1933; *Chem. Abs.*, **28**, 2456 (1934).

[116] Bachhaus, A. A., *Am. Dyestuff Rept.*, **16**, 645, 660 (1927); *Chem. Abs.*, **22**, 127 (1928).

[117] Leboucher, P. J. M., French P. 675,109, Oct. 4, 1928; *Chem. Abs.*, **24**, 2815 (1930).

[118] Rathier, J., *Papier*, **37**, 83 (1934); *Chem. Abs.*, **28**, 2898 (1934).

[119] Allingham, J., U. S. P. 1,553,737, Sept. 15, 1925; *J. Soc. Chem. Ind.*, **44**, 904 (1925).

[120] Kögel, G., U. S. P. 2,068,919, 1937; *Chem. Abs.*, **31**, 1916 (1937).

[121] Gerlach, W., and Schweitzer, E., "Foundations and Methods of Chemical Analysis by Emission Spectra," London, Adam Hilger, Ltd., 123 pp., 1931.

Fitch, A. A.: "Spectrum Analysis in Mineralogy," London, Adam Hilger, Ltd., 52 pp., 1931.

Smith, D. M.: "Bibliography of Literature on Spectrum Analysis," London, British Non-ferrous Metals Research Association, 20 pp.

Crook, W. J.: "Metallurgical Spectrum Analysis," Stanford Univ. Press, 82 pp.

Gerlach, W., and Gerlach, W.: "Clinical and Pathological Applications of Spectrum Analysis, with notes on Spectrography in Chemistry and Mineralogy and Tables for Qualitative Analysis," Leipzig, L. Voss, 1933.

Owens, J. S., *Ind. Eng. Chem. (Anal. Ed.)*, **10**, 64 (1938).

[122] Eddy, C. E., *Chem. Eng. Mining Rev.*, **23**, 309 (1931); *Chem. Abs.*, **25**, 3918 (1931).

[123] Fromherz, H., *Chem. Ztg.*, **60**, 445 (1936).

[124] Henne, A. L., and Clark, G. L., *Compt. rend.*, **184**, 26 (1927); Clark, G. L., and Thee, W. C., *Ind. Eng. Chem.*, **18**, 528 (1926); Clark, G. L., and Henne, A. L., *J. Soc. Automotive Eng.*, **20**, 264 (1927); Clark, G. L., *J. Soc. Automotive Eng.*, **23**, 167 (1928); Clark, G. L., and Smith, H. A., *J. Phys. Chem.*, 659 (1927); Rassweiler, G. M., and Withrow, L., *Ind. Eng. Chem.*, **24**, 528 (1932).

[125] Danckwortt, P. W., "Luminescenz Analyse," Leipzig, Akad. Verlags, 1934.

Bernheim, G., and Guyot, M., "Traite d' analyse par les ultraviolets filtrés." Paris, Maloine, 1932.

Radley, J., and Grant, J., "Fluorescence Analysis in Ultraviolet Light." 2nd. ed., London, Chapman & Hall, 1935.

Haitinger, M., "Die Fluorescenzanalyse in der Mikrochemie." Vienna, Emil Haim & Co.

Déribéré, M., "Les applications pratiques de la luminescence. Fluorescence. Phosphorescence. Lumière noire." Paris. Dunod.

[126] Kögel, G., *Sitzungsber. Preuss. Akad. Wiss.*, **37**, 97 (1914); Fonzes-Diacon, Faucon and Reynaud, *Ann. fals.*, **17**, 20 (1924); Mellet and Bischoff, M. A., *Compt. rend.*, **181**, 868 (1925); Bonacini, C., *Brit. J. Photography*, **75**, 36 (1928); *Chem. Abs.*, **22**, 1737 (1928); Mezger., O., *Chem. Ztg.*, **53**, 965, 985, 1006 (1929); Grant, J., *Analyst*, **58**, 603 (1933); Callo, A., British P. 402,136 (1933); Wood, H. P., U. S. P. 2,016,474 (1935); Mitchell, C. A., *Analyst*, **58**, 532 (1933).

[127] Eibner, A., *Angew. Chem.*, **45**, 301 (1932).

[128] Grant, J., *Analyst*, **59**, 749 (1934).

[129] Mitchell, C. A., *Medical-legal Criminol. Rev.*, 3, 3 (1935).

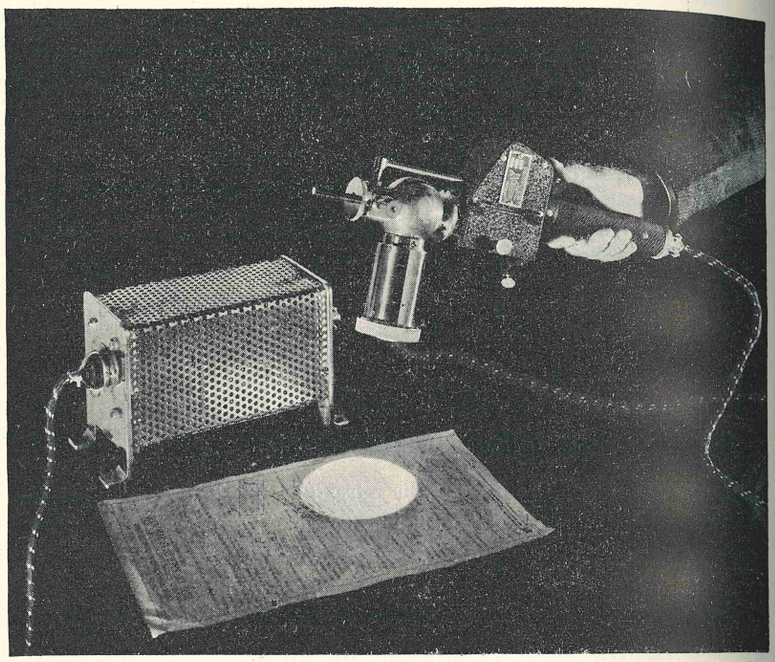
[130] Muir, J., *Ind. Chemist*, **9**, 49 (1933); Grant, J., *Ibid.*, **14**, 277, 289 (1938).

[131] J. Grant, *Ceramic Industry*, 420, June, (1936).

[132] See Carleton Ellis, "The Chemistry of Synthetic Resins," New York, Reinhold Publishing Corp., 1935.

either powder, dry or in solution, exhibit characteristic fluorescence colors which, in some cases, may serve for the identification of the substances. Although minerals are well known to exhibit brilliant colors, it has been shown that various samples of the same mineral may exhibit different colors, so that the importance of the method is receding. It is, however, of value in some cases in the study of the conditions under which the mineral was originally deposited.

The method is not adapted to the identification of organic compounds by a systematic procedure. It has also been shown that many compounds which, like quinine, fluoresce brilliantly, owe this property to the presence of traces of as yet unidentified impurities. Nevertheless, there are many instances in which the method offers considerable aid in the rapid control of technical processes.



Courtesy National Carbon Co., Inc.

FIGURE 131. Eveready Fluoray Apparatus.

In Germany, there was introduced the Hanau "Quarzlampen für Analyse" as a source for this purpose. An apparatus which employs visible light, sunlight or daylight is the Callophane, merely a light-tight box for the specimen, which is illuminated by a filter of special glass on one side of the box and having provision for viewing the specimen under a black cloth thrown over the head of the observer. Figure 131 shows the Eveready carbon arc apparatus (Fluoray) devised for the purpose by the National Carbon Co. A 4-mm. Corning red-purple ultrafilter No. 587 transmits chiefly the 3650A line.

The method is extremely rapid, sensitive and does not alter the object investigated. The personal equation of the observer enters into the color readings to a considerable extent, but recently efforts have been made to adapt the method to a

quantitative recording of the intensities of the fluorescence at various wave-lengths. It is interesting to note that in a rather neglected paper, Desha [133] proposed a method of quantitative analysis by comparative fluorescence (fluorometry).

Since the fluorescence of certain compounds changes with the pH of the solution in which they are dissolved, they can be employed as fluorescent indicators in titrations conducted in the light of a Wood lamp.[134]

The fluorescence methods also may be adapted to microscopic objects. A fluorescence microscope was described by Haitinger and Reich.[135, 136]

It has been proposed by Andant [137] to utilize their Raman spectra in the identification of the hydrocarbons present in gasolines.

[133] Desha, L. J., *J. Am. Chem. Soc.*, **42,** 1350 (1920); see also F. Bandow, *Biochem. Z.*, **295,** 154 (1938).

[134] Déribéré, M., *Documentation sci.*, **6,** 114 (1937); *Chem. Abs.*, **31,** 6086 (1937); *Tiba,* **15,** 349 (1937); *Chem. Abs.*, **32,** 1602 (1938).

[135] Haitinger, M., and Reich, V., *Chem. Fabrik,* 529, 1929; Haitinger, M., "Fluorescenzmikroskopie. Ihre Anwendung in der Histologie und Chemie." Leipzig. Akad. Verlag.

[136] For a detailed discussion of modern theories of fluorescence and phosphorescence, see Pringsheim, P.; "Fluorescenz und Phosphorescenz im Lichte der neueren Atomtheorie," Berlin, J. Springer, 1929.

[137] Andant, A., *Chimie et industrie, Special No. 480,* June, 1933; *Chem. Abs.*, **27,** 5952 (1933).

Part IV
Biological Applications

Chapter 34

The Photochemical Behavior of Compounds of Biological Significance

An understanding of the processes underlying the biological applications of ultraviolet light demands a knowledge of the photochemical behavior of the compounds present in biological systems. Of the three chief classes of biochemical compounds—proteins, carbohydrates and lipids—the carbohydrates are discussed in Chapter 23. The fats are discussed in Chapter 29. Other lipid reactions have been relatively little studied aside from the well-known conversion of the sterols into the D vitamins. Consideration of this process is deferred to Chapter 39.

Lipids

Lecithin solutions, aqueous or alcoholic, absorb radiations in the region of 2970A. Kollath [1] suggested that when skin is irradiated, its lecithin may be the source of some physiologically active substances of which acrolein may be typical. He based this upon the observation that either a very dilute aqueous solution of acrolein or an irradiated aqueous emulsion of lecithin when added to ferrous salts enabled them to aid the growth of the influenza bacillus. Kögel believes irradiation of lecithin or choline by sunlight or ultraviolet light to lessen their power of reducing a silver-metol acetic acid reagent.[2] In the case of lecithin, the acidity increases, because of the liberation of phosphoric and fatty acids, along with glycerol and choline.[3]

Although Becking and Gregersen [4] believed the permeability of membranes made from equal proportions of collodion and lecithins to be transitorily increased by illumination, Brooks [5] considered that this is in need of further experimental support.

The ability of cephalin to protect cholesterol sols from the coagulating action of salts is destroyed by intensive ultraviolet irradiation.[6] An irradiated 0.25 per cent cephalin sol does not flocculate gold sols, differing in this respect from irradiated proteins. Neither does it cause the hemolysis of red blood cells, an effect which has been observed in the case of irradiated lecithin sols by Fabre and Simonnet.[7]

Bile acids no longer give the Nakagawa red reaction after ultraviolet irradia-

[1] Kollath, W., *Klin. Wochschr.*, **6,** 13 (1927); *Chem. Abs.*, **21,** 2009 (1927); see also Spiegel-Adolf, M., *Biochem. J.*, **29,** 2413 (1935).

[2] Kögel, G., *Z. Krebsforsch.*, **46,** 105 (1937); *Chem. Abs.*, **31,** 8670 (1937).

[3] Roffo, A., and Correa, L., *Bol. inst. med. exptl. No. 42* (1936); *Rev. sudamericana endocrinol. immunol. quimiotherap.*, **20,** 548; *Chem. Abs.*, **32,** 201 (1938).

[4] Becking, B. L., and Gregersen, M., *Proc. Soc. Exptl. Biol. Med.*, **22,** 130 (1924); *Chem. Abs.*, **19,** 3273 (1925).

[5] Brooks, S. C., *Science*, **61,** 214 (1925). See also Brauner, L., and Brauner, M., *Protoplasma*, **28,** 230 (1937).

[6] Spiegel-Adolf, M., *J. Am. Chem. Soc.*, **57,** 1431 (1935).

[7] Fabre, R., and Simonnet, H., *Bull. soc. chim. biol.*, **10,** 1036 (1928); *Chem. Abs.*, **24,** 1126 (1930).

tion.[8] Such treatment also reduces the ability of sodium glycocholate to detoxify certain organ poisons (lung or intestine).[9]

On irradiation, methyl cholate in chloroform becomes yellow, shows a decreased rotation, and yields on fractional crystallization, a β-ester of lower rotation and higher melting point. A stereoisomeric change is believed to occur at the secondary hydroxyl group of ring III of the ester. Neither the free acid nor its sodium salt in water suffered the isomerization. The β-ester differed from the original α-form in its greatly retarded Mylius reaction, its greater solubility, and its failure to be precipitated by digitonin. A further product of the irradiation was a resin which on saponification yielded a yellow acid, $[\alpha]_D^{20}=25$, with a titration equivalent of 591.7, and probably a condensation product of cholic acid.[10, 11]

Proteins and Amino-acids

The photochemistry of the proteins is best approached by considering first the behavior of their degradation products, the amino- acids. The absorption of ultraviolet light by proteins is very largely due to their ring-containing amino- acids, tryptophane, phenylalanine and tyrosine.[12] These amino- acids exhibit selective absorption between about 2400 and 2900A, the maximum being at about 2750A, at least in the case of tryptophane.[13] In connection with other investigations, Svedberg and co-workers have given ultraviolet absorption curves for a number of proteins, from which it can be readily shown that the selective absorption with maximum at 2750 to 2800A depends in large part upon the content in the proteins of the amino- acids tryptophane and tyrosine. The influence of most of the remaining amino- acids is evident chiefly in the absorption at wave-lengths of 2300A or less. Of recent years many papers,[14] on details of the absorption spectra of proteins have appeared.[15]

Amino- Acids. Tryptophane and tyrosine are sensitive to irradiation with ultraviolet light, absorbing oxygen under its influence.This accounts for most of the oxygen uptake by irradiated plasma, according to Harris.[16]

[8] Mikami, H., *J. Biochem. Japan,* **14,** 489 (1932); *Chem. Abs.,* **26,** 1968 (1932).

[9] Ito, R., *Folia Pharmacol. Japan.,* **12,** No. 2, 131 (1931); *Chem. Abs.,* **25,** 5507 (1931).

[10] Uraki, Z., *Z. physiol. Chem.,* **207,** 16 (1932); *Chem. Abs.,* **26,** 3802 (1932).

[11] Phosphatides and other lipids are irradiated in a patent of "Pharmagans" Farm. Ins. L. W. Gans, A. G., Kollath, W., and Magistris, H., British P. 311,436, Jan. 10, 1928; *Chem. Abs.,* **24,** 920 (1930).

[12] Harris, F. I., and Hoyt, H. S., *Pathology,* **2,** 245 (1919); *Chem. Abs.,* **13,** 2384 (1919).

[13] Holiday, E. R., *Biochem. J.,* **30,** 1795 (1936); Feraud, K., Dunn, M. S., and Kaplan, J., *J. Biol. Chem.,* **112,** 323 (1935); **114,** 665 (1936); Heidt, L. J., *J. Biol. Chem.,* **115,** 223 (1936). These references give extensive citations to earlier work.

[14] Shibata, Y., and Asahina, T., *Bull. Chem. Soc. Japan,* **1,** 71 (1926); **2,** 324 (1927); Grinbaum, R., and Marchlewski, L., *Bull. intern. acad. polon. sci., Classe sci. math. nat.,* **A,** 156 (1937); *Chem. Abs.,* **32,** 1576 (1938).

[15] Some of the more important are the following: Abderhalden, E., and Haas, R., *Z. physiol. Chem.,* **155,** 195 (1926); Gioh, G., and Weltner, M., *Ibid.,* **198,** 267 (1931); Vles, F., and Prager, M., *Arch. Phys. Biol.,* **10,** 5 (1932); *Chem. Abs.,* **27,** 5643 (1933); Roche, J., and Dubouloz, P., *Compt. rend.,* **196,** 646 (1933); Marchlewski, L., and Wierzuchowska, J., *Bull. Acad. Polonaise,* **A,** 471 (1928); *Brit. Chem. Abs.,* **A,** 459 (1929); Theorell, H., *Biochem. Z.,* **268,** 55 (1934); Giza, T., *Bull. Intern. Acad. Polonaise,* **A,** 421 (1934); *Chem. Abs.,* **29,** 2977 (1935); Porcher, C., Volkringer, H., and Brigando, J., *Lait,* **14,** 1041 (1934); *Chem. Abs.,* **29,** 3697 (1935); Hicks, C. S., and Holden, H. F., *Australian J. Exp. Biol. Med. Sci.,* **12,** 91 (1934); *Chem. Abs.,* **29,** 2556 (1935); Coulter, C. B., Kabat, E. A., and Stone, F. M., *J. Bacteriol.,* **29,** 54 (1935); *J. Gen. Physiol.,* **19,** 739 (1936); Grinstein, M., *Rev. inst. bacteriol. dept. nacl. hig. (Buenos Aires),* **7,** 351 (1936); Mitra, B. N., *Indian J. Med. Research,* **24,** 5 (1936); Almquist, H. J., Givens, J. W., and Klose, A., *Ind. Eng. Chem.,* **26,** 847 (1934); Gioh, J., and Faltin, E., *Z. physiol. Chem.,* **199,** 13 (1931); Gioh, J., and Weltner, M., *Biochem. Z.,* **273,** 389 (1934); Freudenberg, K., Discherl, W., and Eyer, H., *Z. physiol. Chem.,* **187,** 89 (1930); Vles, F., and Cohn, C., *Arch. Phys. Biol.,* **5,** 48 (1926); *Chem. Abs.,* **21,** 2997 (1927); DeBoer, J. H., Dippel, C. J., and Custers, J. F. H., *Rec. trav. chim.,* **52,** 195 (1933); Smith, F. C., *Proc. Roy. Soc.,* **104B,** 198 (1929); Asahina, T., *Bull. Chem. Soc. Japan,* **4,** 202 (1929); **5,** 354 (1930). For a collection of over two hundred curves for the absorption of proteins, carbohydrates and fats, see Ellinger, F., *Tabulae Biologicae,* **12,** 291 (1937).

[16] Harris, D. T., *Biochem. J.,* **20,** 288 (1926).

Berthelot and Amoreux find tryptophane forms indole-3-acetic acid, detectable after ten minutes of mercury arc irradiation of a solution of 0.5 gm. per liter in a quartz flask. The change is retarded by acidification to pH 4.5.[17]

The non-aromatic amino- acids, such as glycine, alanine, valine, leucine, and aspartic acid, either do not show an increased rate of oxidation when irradiated, or show it less readily. Lieben[18] found that sensitizers such as hematoporphyrin increase the oxygen absorption of the aromatic amino- acids in the light of the quartz lamp and even enable them to show some activity in diffused daylight. The velocity of the oxidation is increased by alkalinity and, in the case of tryptophane, by the addition of formaldehyde. When combined in proteins, the destruction of these amino- acids by light is retarded. They are of particular interest because of their possible participation in the mechanism by which the pigment melanin, or a related substance, may be formed during tanning by sunlight.

Arnow[19] finds irradiation to convert *l*-tyrosine into *dopa* (*l*-3,4-dihydroxyphenylalanine), which itself can be destroyed by prolonged irradiation. An oxidase of certain skin cells (the melanoblasts) converts *dopa* into the tan pigment melanin.

The absorption spectra of the aliphatic amino- acids have been interpreted as indicative of a zwitterion structure $^{+}NH_3CH_2COO^{-}$.[20]

The wave-length at which the continuous absorption of the glycine cation, $NH_3^+CH_2COOH$ begins has been considered by Onslow, Foster and Klingler[21] to afford a measure of the energy required for its dissociation into a hydrogen ion and the zwitterion $NH_3^+\cdot CH_2\cdot COO^-$. In water, it begins at the wave-number 51894 and in hydrochloric acid at 51813, corresponding to 146.86 and 146.63 kcal., respectively. The dissociation frequency is regarded as the sum of the limiting frequency of the Balmer series for hydrogen and of a natural vibration frequency of the molecule-ion, the latter term varying in different amino- acids inversely as the square root of the molecular weight of the zwitterion. In alkaline solution, the glycine cation exists as $NH_3^+CH_2COONa$. Dissociation occurs at a wave-number corresponding to 138.59 kcal.

Irradiation with ultraviolet light causes polymerization.

After irradiation by a mercury arc for fifteen hours, a 0.1*N* aqueous glycine solution increased in conductivity from 1.54×10^{-5} to 71.20×10^{-5}. Its pH increased from 4.8 to 7.45. These changes are due to the formation of ammonia as a result of hydrolysis;

$$NH_2CH_2COOH + H_2O \longrightarrow OHCH_2COOH + NH_3$$

Glycolic acid, but no acetic acid, was formed and the occurrence of side reactions was indicated by the evolution of a gas rich in carbon monoxide. The reaction was most rapid, according to Henri, Weismann and Hirschberg,[22] at pH 3, declining with increasing pH to a minimum at pH 6 and then increasing slowly. Although the absorption begins at about 2400A, wave-lengths less than 2205A are required to produce the decomposition. The quantum yields are about 0.09 for glycine, 0.1 for alanine, and 0.06 for the compound betaine. The rate of reaction is much greater in alanyl-glycine than in glycine and in phenylalanine than in alanine.[23]

[17] Berthelot, A., and Amoreux, G., *Compt. rend.,* **206,** 699 (1938).

[18] Lieben, F., *Biochem. Z.,* **184,** 453 (1927).

[19] Arnow, L. E., *J. Biol. Chem.,* **120,** 151 (1937); *J. Phys. Chem.,* **42,** 415 (1938).

[20] Ley, H., and Zschacke, F. H., *Ber.,* **57B,** 1700 (1924); Leuthardt, F., and Pfister, M., *Helv. Chim. Acta,* **16,** 228 (1933); Ueda, H., *J. Chem. Soc. Japan,* **50,** 502 (1929); *Chem. Abs.,* **26,** 91 (1932); Ley, H., and Arends, B., *Ber.,* **61B,** 212 (1928).

[21] Onslow, G. A., Foster, M. L., and Klingler, C., *J. Biol. Chem.,* **103,** 81 (1933).

[22] Henri, V., Weizmann, C., and Hirschberg, Y., *Compt. rend.,* **198,** 168 (1934); **199,** 1205 (1935).

[23] Weizmann, C., Hirschberg, Y., and Bergmann, E., *J. Am. Chem. Soc.,* **60,** 1799 (1938).

Aspartic acid also is hydrolyzed by ultraviolet light.[24] Irradiation of *l*-aspartic acid produces a new absorption band at 2650A, according to Becker,[25] which is not observed in the case of either asparagine or malic or tartaric acids. Becker showed later that both *l*-aspartic acid and *l*-asparagine yield acetaldehyde upon irradiation. The decomposition products of glycylglycine are different. Because of their α-hydroxyl groups, *dl*-serine and *dl*-lactic acid react differently from *dl*-alanine.[26]

The splitting of ammonia from amino- acids as a result of irradiation has also been studied by Lieben and Urban;[27] only the α-amino- group undergoes this reaction. It is greatest in histidine, 88 per cent, and next in cystine, 32.7 per cent. It is twice as great in lysine, 20.9 per cent, as in arginine, 9.4 per cent. The total decomposition of histidine, tyrosine, or tryptophane, as measured colorimetrically, did not agree with the amount of ammonia evolved, indicating the occurrence of secondary reactions, as had been suggested by Weizmann in the case of glycine. Guanidine was resistant and did not evolve ammonia when irradiated. The amino- group in guanine or in anthranilic acid or benzidine is displaced as easily as when it is present in a side chain.

Hippuric acid is very stable in sunlight.[28] The irradiation of hydroxyproline solutions by a quartz lamp produces two new absorption bands at 2570 and 3130A; the latter does not appear if the solid is irradiated.[29]

Ellinger [30] found that irradiation of a 1-per cent solution of histidine hydrochloride by a quartz mercury arc yields traces of a decomposition product detected pharmacologically by its histamine-like action. Histamine is the product of the decarboxylation of histidine. Photocatalysts did not accelerate the rate of the conversion, which, within certain limits, was unaffected by the pH of the solution or by the duration of the irradiation. Further application of radiations of the wavelengths 2970 and 3020A caused a loss of the pharmacological activity of the irradiated solutions. During the irradiation of histidine, changes in the absorption spectra, interpreted as indicative of the decarboxylation of histidine,[31] were observed. Becker,[32] however, pointed out that the similarity of the absorption spectra of histidine and of histamine is such that the optical method is unsuited for following the decarboxylation of histidine. Ellinger [33] later admitted that what he had regarded as the characteristic absorption of histidine hydrochloride in the longer wave-length region of the ultraviolet had been due to the presence of traces of iron compounds as impurities.

Nevertheless, renewed interest in the reaction was aroused by the demonstration by Holtz [34] that histamine is produced by the irradiation of a 1 : 150 solution of histidine at pH 12 in the absence of oxygen. He was able to isolate 7 mg. of histamine, identified by melting point and analysis of the crystalline pictrate, chloroaurate and chloroplatinate, from the products of irradiation of 1 gm. of histidine.

[24] Weizmann, C., Bergmann, E., and Hirschberg, Y., *Ibid.*, **58**, 1675 (1936).
[25] Becker, J. P., *Strahlentherapie*, **50**, 357 (1934); *Chem. Abs.*, **28**, 5338 (1934).
[26] Becker, J. P., *Strahlentherapie*, **52**, 531-537 (1935); *Brit. Chem. Abs.*, **A**, 437 (1936).
[27] Lieben, F., and Urban, F. F., *Biochem. Z.*, **239**, 250 (1931); *Oesterr. Chem. Ztg.*, **37**, 20 (1934).
[28] Enselme, J., and Pozzi, M., *Bull. soc. chim. biol.*, **17**, 283 (1935).
[29] Becker, J. P., *Strahlentherapie*, **48**, 296 (1933); *Chem. Abs.*, **28**, 1064 (1934).
[30] Ellinger, F., *Archiv exp. Path. Pharmakol.*, **136**, 129 (1928).
[31] Ellinger, F., *Biochem. Z.*, **215**, 279 (1929).
[32] Becker, J. P., *Arch. ges. Physiol (Pflügers)*, **228**, 751 (1931).
[33] Ellinger, F., *Biochem. Z.*, **248**, 437 (1932).
[34] Holtz, P., *Klin. Wochschr.*, **12**, 1613 (1933); *Archiv exp. Path. Pharmakol.*, **175**, 97 (1934).

Ellinger [35] had not been able to identify the irradiation products chemically or spectroscopically after the irradiation of histidine, dry or in solution, but observed that the irradiated solution excites the intestine of a guinea pig. The extracts made with hot chloroform also lowered the blood pressure. Since the injection of histamine into the skin is known to lead to the production of an erythema, Ellinger suggested that the erythema of sunburn may be due to the production of a histamine-like substance from histidine in the upper layers of the epidermis. It was possible to obtain considerable amounts of such substances from even the non-irradiated skin of guinea pigs, although such extracts were never more active than those of irradiated samples.

Szendrö [36] maintains that imidazoleacetaldehyde is the material formed in the irradiation of histidine. On the other hand, according to Wrede and Holtz,[37] the irradiation of imidazolylethyl alcohol does not yield depressor substances.

The oxidation of cystine is not induced by irradiation, according to Harris,[38] and cysteine takes up oxygen so rapidly in darkness that any acceleration produced by ultraviolet light is negligible in comparison with that produced in the case of tryptophane or tyrosine.

The energy required for the dissociation of cystine in hydrochloric acid solutions is, from the absorption spectrum, 70.8 kcal.[39] Lieben and Molnar,[40] find that, although both cystine and cysteine do decompose under the quartz mercury arc, the process proceeds much more slowly than in the case of the aromatic amino-acids. In diffused daylight, the destruction of cystine occurs only in an alkaline medium. Since cysteine oxidizes spontaneously in an alkaline solution, its behavior must be studied in an acid medium and for this a photosensitizer, such as hematoporphyrin, is required in daylight. In the arc light, however, there is a slow decomposition in the absence of a sensitizer. Szendrö, Lambert and Wrede [41] claim that *l*-cysteine is formed in 5-per cent yields when cystine is irradiated with ultraviolet light.

Rao and Dhar [42] studied the photo-oxidation of amino- acids in sunlight in the presence of such sensitizers as titanium dioxide, zinc oxide and alumina. The products formed from the aliphatic representatives included aldehydes, carbon dioxide and ammonia. Monoaminodicarboxylic acids acted less readily than the monoaminomonocarboxylic acids. Anthranilic acid gave aniline and carbon dioxide. Ort has given some attention to the catalytic influence which amino- acids may exert upon the oxidation of sugars irradiated in the presence of hydrogen peroxide.[43]

It is apparent from a consideration of the observations recorded in these paragraphs that, although a quartz mercury arc produces certain changes in amino-acids, the radiations available in sunlight or even from artificial sources under the usual conditions of their therapeutic applications, are incapable of affecting the amino-acids other than those which contain an aromatic, indole or imidazole ring.

[35] Ellinger, F., *Archiv exp. Path. Pharmakol.*, **153**, 120 (1930); *Strahlentherapie*, **38**, 521 (1930); *Chem. Abs.*, **25**, 526 (1931).
[36] Szendrö, P., *Arch. ges. Physiol. (Pflüger's)*, **228**, 743 (1931); *Chem. Abs.*, **26**, 1862 (1932).
[37] Wrede, F., and Holtz, P., *Arch. ges. Physiol. (Pflüger's)*, **234**, 432 (1934); *Chem. Abs.*, **28**, 5477 (1936).
[38] Harris, D. T., *Biochem. J.*, **20**, 288 (1926).
[39] Foster, M. L., Anslow, G. A., and Barnés, D., *J. Biol. Chem.* **89**, 665 (1930); Barnés, D., *Anales Soc. Espan. Fis. Quim.*, **28**, 1386 (1930); *Chem. Abs.*, **25**, 2366 (1931).
[40] Lieben, F., and Molnar, E., *Biochem. Z.*, **230**, 347 (1931).
[41] Szendrö, P., Lambert, V., and Wrede, F., *Z. physiol. Chem.*, **222**, 16 (1933).
[42] Rao, G. G., and Dhar, N. R., *J. Indian Chem. Soc.*, **11**, 617 (1934); *Chem. Abs.*, **29**, 1326 (1935).
[43] Ort, J. M., *J. Phys. Chem.*, **33**, 825 (1929).

In general, there is, on the irradiation of amino- acids with light of sufficiently short wave-length, an evolution of ammonia and a shift of the absorption spectrum to somewhat longer wave-lengths.[44]

The optical rotations of optically active dipeptides are unaltered by exposure to ultraviolet light, but solutions of the corresponding 2,5-diketopiperazines show a diminution in rotation which soon reaches a constant value. Traces of ammonia and carbon dioxide can be detected after irradiation in air, but not in nitrogen, so that the mechanism probably involves oxidation. Solutions of silk peptones show similarly altered rotations.[45]

The irradiation of a solution of Witte's peptone produces a skin on the surface. This skin fails to give the biuret reaction. The tyrosine content is reduced, as is that of histidine and there is no tryptophane present. Since the amino-nitrogen content in this skin is found to be reduced, it is probable that the production of plasteins may have occurred. The minimum amount of skin is formed at pH 5.5. On removal of the film, a new one forms on further irradiation. Solutions of the peptones from casein or silk fail to behave in a similar manner.[46]

Behavior of Proteins on Irradiation.[47] In 1913, Bovie [48] reported that fresh egg albumin, on exposure in a quartz tube at 10 cm. from a mercury arc lamp at room temperature, began to show a feathery coagulum on the walls nearest the lamp and after 35 hours had become fully coagulated and possessed a peculiar, strong odor. When an aqueous solution was employed, less time was required for the coagulation. The product formed settled to the bottom of the tube. Crystalline albumin not freed from ammonium sulfate coagulated more rapidly than fresh egg-white. After dialyzing away the salt, the protein was still more sensitive and showed some coagulation even when exposed in glass tubes. Ox-serum was also coagulated in quartz tubes. No coagulation occurred at zero, but if the solution was then warmed a few degrees it became turbid. If the temperature was then quickly reduced, the solution again became clear. It was suggested that light alters the protein at low temperatures, but that only at higher temperatures does there occur a second change leading to the production of a visible coagulum.[49]

Many observations have since been made of the phenomenon. In the case of serum albumin, Teichler,[50] believed the coagulating action, although not the primary photochemical process, to be dependent upon the relative amounts of sodium and calcium ions present.

The question has been frequently raised as to whether the mechanism is the same as that of the coagulation by heat. Bovie believed this to be the case, since he found the coagulated material soluble in dilute alkali, but insoluble in alcohol, water or dilute acid. Spiegel-Adolf and Krumpel.[51] found that the absorption spectrum changes during heat coagulation in a manner similar to that during

[44] Allen, A. J., Steiger, R. E., Magill, M. A., and Franklin, R. G., *Biochem. J.*, **31**, 195 (1937); Magill, M. A., Steiger, R. E., and Allen, A. J., *Biochem. J.*, **31**, 188 (1937).

[45] Abderhalden, E., and Haas, R., *Z. physiol. Chem.*, **155**, 195, 200 (1926); **166**, 78 (1927); **160**, 256 (1926); **164**, 1 (1927); Hünecke, H., *Ber.*, **60B**, 1451 (1927); Ley, H., and Arends, B., *Ber.*, **61B**, 212 (1928); Abderhalden, E., and Rossner, E., *Z. physiol. Chem.*, **176**, 249 (1928); **178**, 156 (1928); Asahina, T., *Bull. Chem. Soc. Japan*, **4**, 202 (1929); Guthmann, H., Schwerin, K., and Stähler, F., *Strahlentherapie*, **39**, 401 (1931); *Chem. Abs.*, **25**, 2448 (1931).

[46] Lieben, F., and Jesserer, H., *Biochem. Z.*, **275**, 367 (1935).

[47] This subject has been reviewed in considerable detail by Arnow, L. E., *Physiol. Revs.*, **16**, 671 (1936).

[48] Bovie, W. T., *Science*, **24**, 374 (1913).

[49] Bovie, W. T., and Hughes, D. M., *J. Gen. Physiol.*, **1**, 323 (1919); Bovie, W. T., and Klein, A., *Ibid.*, **1**, 331 (1919); Bovie and Daland, G. A., *Am. J. Physiol.*, **66**, 55 (1923).

[50] Teichler, G., *Arch. ges. Physiol (Pflüger's)*, **227**, 558 (1931); *Chem. Abs.*, **25**, 4289 (1937).

[51] Spiegel-Adolf, M., and Krumpel, O., *Biochem. Z.*, **208**, 45 (1929).

irradiation, but that the changes were quantitatively less in the former case. However, Spiegel-Adolf found also, at least in the case of serum albumin,[52] that the coagulum formed by irradiation differed from that formed by heat in not being rendered water-soluble by dilute alkali followed by dialysis. After irradiation in the presence of hydrochloric acid, serum albumin can be salted out, but this differs from the behavior on heating in the presence of acid. In spite of these differences, serum albumin heated or irradiated in the presence of sodium hydroxide shows the same behavior to neutral salts. The presence of larger concentrations of neutral salts does not prevent the coagulation of serum albumin during irradiation, but the presence of multivalent ions does inhibit the precipitation. Potassium thiocyanate does not inhibit the irradiation coagulation and cannot bring the product into solution, differing in this respect from its effects on heat coagulaton.

Clark [53] pointed out that only at pH values near the isoelectric point is albumin coagulated by either light or heat. At other pH values, it remains clear on irradiation but has been altered by the process so that it behaves toward electrolytes as a globulin. Other workers, notably Abderhalden, observed that a slight decrease in pH occurs during the irradiation of globulin and, in the presence of sodium chloride, albumin solutions. The optical rotation also decreases, but the conductivity increases slightly. The increase in acidity was also observed by Mond,[54] who found the viscosity increased, and the surface tension decreased. The latter effect was less in the case of albumin than of globulin.[55]

Stedman and Mendel [56] extended the investigations to about twelve purified proteins. In general, there was a lowering of the coagulation temperature, together with the production of an odor and a yellow tint, and in some cases, an increase in the specific rotation. These changes were independent of the presence of water, electrolytes and oxygen. In tests of some fourteen proteins, it was found by Spiegel-Adolf and Pollaczek [57] that bacterial contamination of the solutions retarded their coagulation during irradiation. The retarding effect persisted even after the infection had spontaneously died.

Rajewsky [58] found the primary denaturation process independent of temperature, only the conglomeration of the denatured particles being accelerated by a rise in temperature. Gentner and Schwerin [59] followed the coagulation by following the changes in the number of particles exhibiting Brownian movement. At the isoelectric point of egg albumin, three processes rather than two may be recognized as involved in the mechanism of coagulation, according to Clark.[60] Following the primary photo-denaturation, she believes there ensues a reaction between the denatured molecule and water, following which there is a flocculation of the denatured molecules to form the coagulum. The first denaturation is a monomolecular process, which, in agreement with Rajewsky, is independent of temperature. The reaction with water has, however, a high temperature coefficient—over ten. The reaction occurs rapidly at 40°C., a temperature at which heat denatura-

[52] Spiegel-Adolf, M., *Biochem. Z.*, **186**, 181 (1927).

[53] Clark, J., *Am. J. Physiol.*, **73**, 649 (1925).

[54] Mond, R., *Arch. ges. Physiol. (Pflüger's)*, **196**, 540 (1922); **200**, 374 (1923); *J. Chem. Soc.*, **123**, and **124**, (I), 868.

[55] Other early observations of this type were due to Schanz, F., *Archiv ges. Physiol. (Pflüger's)*, **164**, 445 (1916); *Chem. Zentr.* **87**, II, 670 (1916); *Chem. Abs.*, **10**, 1656 (1916), and to Kreibich, C., *Arch. Path. Anat.*, **222**, 28 (1916); *Chem. Abs.*, **14**, 2023 (1920).

[56] Stedman, H. L., and Mendel, L. B., *Am. J. Physiol.*, **77**, 199 (1926).

[57] Spiegel-Adolf, M., and Pollaczek, K. F., *Biochem. Z.*, **214**, 175 (1929).

[58] Rajewsky, B., *Biochem. Z.*, **227**, 372 (1930); *Klin. Wochschr.*, **10**, 1673 (1931).

[59] Gentner, W., and Schwerin, K., *Biochem. Z.*, **227**, 286 (1930).

[60] Clark, J., *J. Gen. Physiol.*, **19**, 199 (1935).

tion is inappreciable. Mirsky and Pauling [61] suggest that the primary absorption process causes a break in the native protein molecule which enables it to suffer denaturation at a temperature lower than that otherwise required.

Little is known as yet of the precise nature of this primary process. Lampert and Wels [62] noted during irradiation in the absence of oxygen the formation of a substance with sulfhydril reactions which cannot, however, be separated from the proteins by ultrafiltration or by precipitating the protein with colloidal ferric hydroxide. Mirsky and Anson [63] observed that the number of sulfhydril groups in egg albumin coagulated by ultraviolet light is equivalent to that in samples coagulated by typical denaturing agents.

Other observations of chemical decompositions involved have been occasionally made. Hoffmeister [64] claims that after five hours of irradiation of serum albumin and peptone, the values for acetaldehyde were as high as 68 and 108 mg., respectively, as compared with 18 and 8 mg. in non-irradiated controls. Howitt [65] also suggested that formaldehyde or some similar substance is produced from egg albumin, and that this, by reacting with amino- groups, might account for an observed increased acidity. An alkaline reaction favors the last step and tends to lessen the possibility of a reducing action by the aldehyde.

Gelatin and globin (and also the alkaloid caffeine), when irradiated in weakly acid solutions, yield ammonia, according to Eckstein and Lieben.[66] These observers do not believe an increase in amino- nitrogen to be due to a cleavage of peptide linkages, since peptides are not hydrolyzed under these conditions. They also exclude arginine as the source and believe that both the ammonia and the increased amino-nitrogen originate from the heterocyclic rings of histidine, proline and hydroxylproline. Lieben and Jesserer,[67] however, admit that the peptide linkages in proteins may be less resistant than they are in peptones and peptides, so that it may not be necessary to conclude that the origin is exclusively the breaking of heterocyclic rings.

Much attention has been devoted to the changes wrought by irradiation in the collodial behavior of the proteins. Mond [68] believed that the stability of solutions of serum globulin and fibrinogen are increased since their coagulation temperatures were raised.

According to Cossu,[69] non-irradiated samples of serum albumin show a minimum in the surface tension-pH curve at the isoelectric point, but after irradiation there is a maximum at the isoelectric point and another at a point on the acid side. The protein is no longer stable at the isoelectric point as shown by the fact that the solutions are slightly turbid.

Monomolecular albumin films on irradiation dissolve completely in about two hours.[70] Mitchell [71] found that the phase-boundary potentials of egg albumin films increase when irradiated by the 2537A line. The solid film liquefies. It was suggested that certain CO—NH linkages in the main polypeptide film may be hydrolyzed. It could be shown that this linkage is broken in stearic anilide to the extent of at least 95 per cent, the quantum yield being unity, but varying with the molecular orientation in a manner for which a theory was given. Mitchell called attention to the interesting possibilities offered in biological work by the fact that the photochemistry of monomolecular layers offers a means of studying the effects of orientational factors.

[61] Mirsky, A. E., and Pauling, L., *Proc. Nat. Acad. Sci.*, **22**, 439 (1936).
[62] Lampert, U., and Wels, P., *Archiv exp. Path. Pharmakol.*, **175**, 554 (1934).
[63] Mirsky, A. E., and Anson, M. L., *J. Gen. Physiol.*, **19**, 427 (1936). See also Wenig, K., and Jirovec, O., *Biochem. Z.*, **295**, 405 (1938).
[64] Hoffmeister, A., *Z. physiol. Chem.*, **205**, 183 (1932).
[65] Howitt, F. O., *Nature*, **125**, 412 (1930).
[66] Eckstein, H. C., and Lieben, F., *Biochem. Z.*, **263**, 366 (1933).
[67] Lieben, F., and Jesserer, H., *Biochem. Z.*, **275**, 367 (1935).
[68] Mond, R., *Archiv ges. Physiol. (Pflüger's)*, **196**, 540 (1922); **200**, 374 (1923); *J. Chem. Soc.*, 123-4, 868 (1923).
[69] Cossu, F., *Bull. soc. ital. biol. sper.*, **10**, 973 (1935); *Chem. Abs.*, **30**, 2589 (1936).
[70] Rideal, E. K., *Kolloid-Z.*, **61**, 218 (1932).
[71] Mitchell, J. S., *Proc. Roy. Soc.*, **A155**, 696 (1936).

Among the most carefully conducted and detailed studies of the changes occurring in proteins are those of Spiegel-Adolf.[72] With Krumpel,[73] she showed irradiation to increase the ultraviolet absorption of solutions of electrolyte-free serum albumin in the region 4000 to 2675A, without affecting the location of the absorption maxima and minima. Oxygen was not necessarily present in order to produce these changes. Pseudo-globulin and serum itself also exhibit an increase in absorption when irradiated in the presence of alkali, but euglobulin does not. Egg albumin behaves as does serum albumin.[74] If acid or alkali is added before the irradiation, the increase in absorption increases with the concentration of the added acid or alkali. The effects are much less marked when x-ray or radium irradiation is employed. However, in the presence of materials which under x-radiation fluoresce in the ultraviolet region, the effects of x-rays are similar to those of ultraviolet rays.

Wels [75] found the bluish fluorescence of serum euglobulin under ultraviolet irradiation to be increased after irradiation with unfiltered ultraviolet rays.

Spiegel-Adolf [76] found also that after removing ultraviolet-coagulated serum globulin from a dilute solution, the filtrate contained a substance, probably proteose in nature, which coagulates a sol of colloidal gold. When a concentrated solution of this substance is added to spinal fluid, the mixture simulates the fluid of cases of general paralysis in the diagnostic colloidal gold precipitation test. She also showed that, after irradiation, gelatin solutions lose their protective power for gold sols and tend instead to precipitate them.[77] Arginine, histidine, lysin and choline flocculate colloidal gold only after irradiation, whereas glycine and the cyclic amino- acids do not acquire this property even after irradiation. The ability of histamine solutions (0.00018 mg. per cc.) to precipitate gold sol is lost on irradiation, although not at the same rate at which the pharmacological properties of this compound are lost. Irradiation also destroys the protective power of thymonucleic acid which becomes, like cytosine and uracil, a gold sol precipitant. Exposures up to six hours are required, however.

It has been claimed that differences between globulins and albumins exposed to ultraviolet light for varying periods, 45 minutes, 3 hours and 6 hours, can be demonstrated by the biological reaction of Abderhalden.[78] The enzymes produced by an animal in the Abderhalden reaction after the injection of such products are claimed to be specific for the kind of protein and its exposure time. It also is claimed that irradiation increases the susceptibility of globulin but not of albumin to the action of gastric juice.

[72] A summary is given in *Arch. Path.*, **12**, 533 (1931).
[73] Spiegel-Adolf, M., and Krumpel, O., *Biochem. Z.*, **190**, 28 (1927); *Klin. Wochschr.*, **7**, 1592 (1928); *Biochem. Z.*, **197**, 197 (1928).
[74] Spiegel-Adolf, M., and Oshima, Z., *Biochem. Z.*, **208**, 32 (1929); compare Spiegel-Adolf, M., and Krumpel, O., *Ibid.*, 45, for the effects of heat on absorption.
[75] Wels, P., *Arch. ges. Physiol. (Pflüger's)*, **219**, 738 (1928).
[76] Spiegel-Adolf, M., *Biochem. J.*, **28**, 372 (1934).
[77] Spiegel-Adolf, M., *Biochem. J.*, **28**, 1201 (1934).
[78] Abderhalden, E., and Buadze, S., *Fermentforschung*, **14**, 295 (1934); *Chem. Abs.*, **28**, 6739 (1934).

Early work of Harris [79] indicated that oxygen is absorbed during the irradiation of egg albumin, casein and edestin, but not of gelatin. At the same time, the characteristic absorption maximum at 2800A disappears, at least in the case of egg albumin, according to Becker and Szendrö.[80] Hematoporphyrin and chlorophyll greatly accelerate the velocity of oxidation of plasma in light. This is true also, but to a lesser degree, of a number of dyes, such as methylene blue and eosin, and of ionic iron.[81]

Wels demonstrated [82] that the irradiation of egg albumin in an atmosphere of nitrogen leads to the production of a substance which can be readily oxidized by oxygen or by methylene blue. This converts the substance into an oxidant capable of oxidizing the yellow leucobase of the red dye, Rosindulin GG. Irradiation under decreased oxygen tension instead of under nitrogen decreases but does not entirely prevent the formation of the substance which reduces methylene blue. After irradiation in oxygen at higher tensions, the substance is produced only in the oxidant form, capable of oxidizing the leuco-rosindulin but not of reducing methylene blue. Wels concluded from these observations that irradiated skin is the source of a substance analogous to the sulfhydryl compounds and which may play a part in tissue respiration. The property of bleaching methylene blue not shown by protein irradiated in an oxygen stream may be acquired by keeping the solution for a few hours in contact with washed frog muscle or its dry powder. The dry muscle powder bleaches methylene blue very slowly; if it is irradiated in nitrogen,[83] and oxidized protein is added, the bleaching is accelerated four times. Non-irradiated protein does not act.

That the reduction-oxidation potential of solutions of egg and serum albumins is reduced by coagulation either by heat or ultraviolet light has also been observed by Nakamura.[84] Kather [85] states that ultraviolet-irradiated egg albumin forms a copper-complex which is five to ten times as active as that from the non-irradiated protein in catalyzing the oxidation of unsaturated acids.

Fibrinogen is precipitated from its solutions by irradiations. Such irradiated solutions are no longer coagulated by the toxin of *Crotalus terrificus*.[86] The action of the ultraviolet light on this globulin is inhibited by the presence of hematoporphyrin.[87]

Dried hide powder, after several weeks of irradiation by a quartz mercury arc, either in air or in a quartz tube under nitrogen, acquires a bright canary yellow color. Of the irradiated powder, 27.8 per cent dissolves in an equal weight of water at room temperature. The capacity of hide powder to combine with hemlock tannin at pH 3.8 is greatly reduced by the irradiation.[88]

Keratin, as in unbleached horn, after ultraviolet irradiation, assumes in a lead nitrate solution a deeper color than that given by the non-irradiated sample. Wool shows a similar behavior. Thus only after irradiation do bleached horn and bleached wool acquire the ability to form lead sulfide with solutions of lead salts.[89]

[79] Harris, D. T., *Biochem. J.*, **20**, 288 (1926).
[80] Becker, J. P., and Szendrö, P., *Arch. ges. Physiol. (Pflüger's)*, **228**, 755 (1931).
[81] Harris, D. T., *Biochem. J.*, **20**, 280 (1926).
[82] Wels, P., *Arch. exp. Path. Pharmakol.*, **171**, 480 (1933); *Chem. Abs.*, **27**, 5344 (1933).
[83] Wels, P., and Hesse, R., *Naturwiss.*, **22**, 648 (1934).
[84] Nakamura, Y., *J. Agr. Chem. Soc. Japan*, **11**, 1101 (1935); *Brit. Chem. Abs.*, **A**, 360 (1936).
[85] Kather, E., *Arch. exp. Path. Pharmakol.*, **184**, 645 (1937); *Brit. Chem. Abs.*, **A** (III), 253 (1937).
[86] Arthus, M., and Boshell, G., *Arch. intern. physiol.*, **30**, 244 (1928); *Brit. Chem. Abs.*, **A**, 1024 (1929).
[87] Howell, W. H., *Arch. intern. physiol.*, **18**, 269 (1921); *Chem. Abs.*, **16**, 935 (1922).
[88] Thomas, A. W., and Foster, S. B., *J. Am. Leather Chem. Assoc.*, **20**, 490 (1925).
[89] Beutel, E., and Kutzelnigg, A., *Monatsh.*, **64**, 183 (1934).

It is assumed that a part of the sulfur of keratin is converted into sulfur ions under the influence of light. On the other hand, Barritt and King [90] state that on exposure to ultraviolet radiations wool loses part of its sulfur as sulfur dioxide, which may be evolved, adsorbed or oxidized to sulfuric acid. From x-ray observations, Astbury and Woods [91] state that irradiation of unstretched keratin by ultraviolet light or x-rays causes intramolecular changes analogous to those due to the action of water on stretched keratin.

It has been claimed that when gelatin is irradiated, it is altered in such a way as to lessen its tendency to swell in water. The effect is said to be proportional to the duration of illumination.[92] The solubility of the swollen gelatin in water is reduced, and the irradiated solution has the property of reducing ammoniacal silver nitrate solution, but the elementary analysis is unaffected. The presence of oxygen during the irradiation is not essential. The effects of irradiation may be lessened by careful purification of the gelatin, and it has been suggested that an iron sensitizer found in the ash may be necessary for the process. Sheppard and Houck [93] believe the underlying reaction to be of termolecular order. According to Ponthus [94] irradiation increases the electrical conductivity and decreases the optical density and viscosity of gelatin, but does not change its state of aggregation. Duce [95] finds the surface tension to be lowered and attributes this effect to a decrease in the hydration of the colloidal particles.

Insulin is not resistant to ultraviolet rays in the presence of oxygen and it cannot, therefore, be sterilized by them.[96] Variations observed in the effect of these radiations on commercial insulin preparations have been attributed to variations in their content of phenol, which protects the preparation against their action.[97] According to Ellis and Newton,[98] exposure of commercial insulin in nitrogen in a quartz tube for 19 to 48 hours destroys the active hypoglucemic substance. Substances remain which, when injected, have the property of increasing the blood sugar level. Ozone and oxygen in sunlight destroyed the hypoglucemic substance in insulin solutions but did not develop the substances producing the increase in blood sugar in one hour.[99]

Freudenberg and Wegmann [100] find that the activity of irradiated insulin can be partly restored by oxidation by hydrogen peroxide in the presence of cysteine. Irradiated egg-white inactivates insulin in an atmosphere of nitrogen. The photochemically liberated sulfhydryl groups reduce the active disulfide form of insulin to the inactive sulfhydryl form.[101] The reducing properties may be developed in protein even by therapeutic doses of irradiation.[102]

In the presence of quinones as sensitizers, hemoglobin (and also chlorophyll)

[90] Barritt, J., and King, A. T., *J. Textile Inst.*, **20**, 151T, 159 (1929); *Brit. Chem. Abs.*, **B**, 846 (1929).
[91] Astbury, W. T., and Woods, H. J., *Phil. Trans.*, **32**, 333 (1933).
[92] Brintzinger, H., and Maurer, K., *Kolloid.-Z.*, **41**, 46 (1927).
[93] Sheppard, S. E., and Houck, R. C., *J. Phys. Chem.*, **36**, 2885 (1932).
[94] Ponthus, P., *Compt. rend.*, **196**, 1248 (1933).
[95] Duce, W., *Arch. ital. biol.*, **94**, 34 (1935); *Boll. soc. ital. biol. sper.*, **10**, 978 (1935); *Chem. Abs.*, 30, 2454 (1936); Kronenberger, P., *Boll. soc. ital. biol.*, **9**, 1336 (1934).
[96] Cazzini, U., *Biochem. terap. sper.*, **16**, 563 (1929); *Chem. Abs.*, **24**, 917 (1930); Den Hoed, D., De Jongh, S. E., and Peek, A., *Biochem. Z.*, **205**, 144 (1929).
[97] Küstner, H., and Eissner, W., *Klin. Wochschr.*, **11**, 1668 (1932); *Chem. Abs.*, **27**, 779 (1933).
[98] Ellis, M. M., and Newton, E. B., *Am. J. Physiol.*, **73**, 530 (1925).
[99] Keeser, E., [*Arch. exp. Path. Pharmakol.*, **166**, 624 (1932); *Chem. Abs.*, **26**, 5582 (1932)] believes irradiation with green or blue light to activate insulin, although red light partially destroys its activity.
[100] Freudenberg, K., and Wegmann, T., *Z. physiol. Chem.*, **233**, 159 (1935).
[101] Kather, E., *Arch. exptl. Path. Pharmakol.*, **185**, 323 (1937); *Chem. Abs.*, **32**, 6267 (1938).
[102] Kämmerling, I., *Arch. exptl. Path. Pharmakol.*, **186**, 434 (1937); *Chem. Abs.*, **32**, 8448 (1938).

absorb hydrogen under the influence of light.[103] Oxidation occurs subsequently, turning the quinones (with the exception of juglone), brown. In sunlight, hemoglobin is degraded into its decomposition products, the process being accelerated by the use of glutathione as sensitizer. Under these conditions, chlorophyll may be destroyed.[104] Lennox[105] states that in ultraviolet light, potassium iodide, but not free iodine, accelerates the conversion of hemoglobin to methemoglobin. Etioporphyrin I, when irradiated in pyridine containing sodium ethylate, alters its spectrum, a new absorption band appearing at 6360A, the red solution becoming blue and then green.[106] Oxygen is necessary for the change to occur. The solution contains etioglaucobilin and a red diketone of this substance, besides a mixture of dinuclear aldehydes, very similar to etioneoxanthomethenes. The first step in the photochemical oxidation is the addition of oxygen at several of the methine bridges of the porphyrin. The resulting peroxide isomerizes and the bridge breaks to yield an isomer of glaucobilin, which rearranges. The other products result from other rearrangements of the peroxide.

Enzymes

Since the activity of an enzyme depends, in general, upon the integrity of its colloidal protein component, the destruction of the activity of enzymes is intimately bound up with the effects of ultraviolet upon the proteins. Since, however, there may conceivably be various prosthetic groups in the enzyme molecule which also condition its activity, the details of the destruction process may be expected to vary from enzyme to enzyme. Therefore, although most enzymes which have been tested have been found to be sensitive to ultraviolet rays, the behavior of each must be discussed separately. In many cases the activity of enzymes depends also upon the presence of specific coenzymes, and these also may be affected by radiations.[107]

It has been claimed that certain monochromatic radiations in the visible range increase the activity of catalase, pepsin, trypsin, and lipase. In no case was the enzyme activity depressed.[108]

Application of ultraviolet rays may aid in determining the unitary or non-unitary nature of certain enzymes which have the property of acting upon more than one substrate. If the activity toward each is destroyed at the same rate on irradiation of the preparation it may be assumed that but one enzyme is involved, according to Helferich and Brieger.[109] In the emulsion of almonds, the activity toward phenol β-*d*-glucoside and phenol-*d*-galactoside diminish at the same rate, suggesting that both substrates are hydrolyzed by the same enzyme. The activity toward phenol -β-*d*-glucoside, however, diminished twice as rapidly as that toward phenol α-*d*-mannoside, suggesting that different enzymes affect these substrates.[110]

Diastase. The behavior of this enzyme has been extensively studied by Pincussen. It is not destroyed by sunlight, but is inactivated by shorter ultraviolet

[103] See also Gouzon, B., *Ann. physiol. physicochim. biol.*, **11**, 388 (1935).

[104] Kögel, G., *Strahlentherapie*, **42**, 379 (1931); *Brit. Chem. Abs.*, **A**, 634 (1932).

[105] Lennox, F. G., *Australian J. Exptl. Biol. Med. Sci.*, **13**, 193 (1935); *Brit. Chem. Abs.*, **A**, 92 (1936).

[106] Fischer, H., and Herrle, K., *Z. physiol. Chem.*, **251**, 85 (1938).

[107] An early attempt to classify enzymes in accordance with their sensitivity to ultraviolet under various conditions was made by Agulhon, H., *Compt. rend.*, **153**, 979 (1911).

[108] Keeser, E., *Arch. exp. Path. Pharmakol.*, **164**, 626 (1932); *Chem. Abs.*, **26**, 3269 (1932); note also Collier, H. B., and Wasteneys, H., *Australian J. Exp. Biol. Med. Sci.*, **9**, 89 (1932); *Chem. Abs.*, **27**, 2164 (1933).

[109] Helferich, B., and Brieger, G., *Z. physiol. Chem.*, **221**, 94 (1933); Helferich, B., Rohr, H., and Günther, E., *Ibid.*, 90.

[110] Note also Hill, K., *Ber. für Handlung. Sachs. Akad. Wiss. Leipzig, Math. Phys. Klasse*, **86**, 115 (1934); *Chem. Abs.*, **28**, 5843 (1934).

rays. The destruction is greatest at pH 4.6 at which the enzyme also exhibits its maximum activity. The destruction is least at pH 7.0 and 7.4.[111] The rate is accelerated by the presence of iodides and inhibited by glycine and by starch, but is but little affected by sugars or by change of temperature. In the presence of dextrose, sunlight may have a slight effect. The inactivation of 0.1-per cent malt diastase acting on 1-per cent starch solution at varying pH values proceeds as a unimolecular reaction, although in the presence of 0.5 per cent of starch only the later stages of the reaction are expressed by the unimolecular rate equation. The disagreement is still more marked in the presence of 0.25 per cent of starch. A 0.2-per cent solution of the enzyme gives complex results in the presence of either 1-, 0.5- or 0.25-per cent starch solutions.[112]

Phosphate solutions (6*M*) protect malt diastase and the maltase of pancreatin from inactivation by ultraviolet rays, but less dilute solutions are less effective. Similar results are given by acetate solutions of the same pH. In the presence of a phosphate buffer, with or without the addition of sodium chloride, the protective action is at a maximum at pH 6.64.[113] Ammonium, potassium and lithium chlorides, potassium bromide and sodium fluoride protect Taka-diastase to varying degrees, the effects being more marked in dilute solutions of these salts than in more concentrated ones. Potassium and sodium nitrates and nitrites give similar results but do not show the same varying effects at different temperatures.

Lüers and Lorinser[114] found the inactivation of malt amylase by ultraviolet rays followed neither the mono- nor bi-molecular reaction equations or the Schütz law. The temperature coefficient is 1.30 between 20 and 30°C.

Pincussen[115] believed also that in alkaline solutions, irradiation increases the action of salivary and Taka-diastases, pancreatic diastases showing a similar but very much less marked response.

During the progressive purification of diastase from the pancreas, the sensitivity toward ultraviolet rays progressively increases.[116] Diastase which had been rendered almost inactive by irradiation could be partly reactivated by the addition of small quantities of non-irradiated diastase. Since this effect is not obtained in the case of heat inactivation, the mechanisms of the two modes of inactivation were thought different.[117]

Although Kawakami[118] was unable to confirm the inactivation of Taka-diastase by ultraviolet rays, Thompson and Hussey[119] found the inactivation of amylase to follow a unimolecular course for 88 per cent of the process. Similar results were recorded for Taka-diastase in 0.1-per cent solution by Yamashiki.[120] The influence of the voltage at which the mercury arc was operated upon the value of the monomolecular rate constant was determined by Thompson and Tennant[121] for pancreatin solutions. With 4 amperes and a potential of 75 volts, 0.02-per cent pancreatin solution at pH 6.7 gave a constant of 0.259. With 70 volts across the

[111] Pincussen, L., *Biochem. Z.*, **134**, 459 (1923); *J. Soc. Chem. Ind.*, **42A**, 370 (1923).

[112] Pincussen, L., and DiRenzo, F., *Biochem. Z.*, **144**, 366 (1924).

[113] Pincussen, L., *Biochem. Z.*, **144**, 372 (1924); see also Terroine, E. F., and Bonnet, R., *Bull. soc. chim. biol.*, **9**, 982 (1927); *Chem. Abs.*, **22**, 1169 (1928).

[114] Lüers, H., and Lorinser, P., *Biochem. Z.*, **144**, 212 (1924).

[115] Pincussen, L., *Biochem. Z.*, **152**, 406 (1924).

[116] Pincussen, L., *Fermentforschung*, **8**, 181 (1925); *Biochem. Z.*, **171**, 1 (1926). Note also Kambayashi, Y., *Biochem. Z.*, **203**, 334 (1928).

[117] Pincussen, L., and Oya, T., *Biochem. Z.*, **207**, 410 (1927).

[118] Kawakami, T., *J. Pharm. Soc. Japan*, **49**, 361 (1929); *Chem. Abs.*, **23**, 4238 (1928).

[119] Thompson, W. R., and Hussey, R., *J. Gen. Physiol.*, **15**, 9 (1931).

[120] Yamashiki, H., *Acta Schol. Med. Univ. Imp. Kyoto*, **16**, 365 (1934); *Chem. Abs.*, **28**, 4759 (1934).

[121] Thompson, W. R., and Tennant, R., *J. Gen. Physiol.*, **18**, 675 (1935).

lamp it was reduced to 0.172 and with 80 volts it was raised to 0.302. The protective action of added dog serum on the stability of the solutions could be accounted for by internal filtering without the necessity of assuming for the serum a specific negative catalytic action.

Sensitizers like eosin, sodium anthraquinone disulfonate and sodium dichloroanthracene disulfonate aid various photochemical processes but have only a depressing effect upon the inactivation of Taka-diastase by ultraviolet light. Potassium ions increase the effects of light and decrease the rate of heat inactivation; the reverse is true of the calcium ion.[122]

Diastase also may be protected from the action of ultraviolet light by the presence of asparagine, anilinoacetic acid, ammonium citrate, gelatin or tyrosine, probably by internal filtering.[123]

Hutchinson and Ashton[124] found that full ultraviolet irradiation retards the ability of both salivary and malt diastases to produce dextrin and sugars from starch in an inverse relation to the intensity of the light used. They report also that green light had a somewhat similar effect on salivary diastase, but that both salivary and malt preparations were stimulated in their activity by either red-yellow or near ultraviolet light. Apparent differences of the rates of production of dextrins and of maltose by malt diastase during irradiation with various monochromatic radiations led them to suspect the presence of different enzymes in the preparation.

Tang and Sung[125] find fully germinated malt unaffected by ultraviolet rays, although malt which had just begun to germinate lost its activity on irradiation.

Sucrase. Preparations of this enzyme exhibit an absorption band with its maximum at about 2700A, attributed to the presence of tryptophane in the protein of the enzyme. Addition of this amino- acid protects[126] the enzyme from inactivation by ultraviolet light. Yeast gums also present in the preparations have but very little absorption at 2700A.

Although yeast autolyzates are almost uninjured by irradiation for two hours, sucrase preparations of a high degree of purity were inactivated within twenty to thirty minutes.[127] The pH had but slight effect on the course of inactivation. The curve was linear during the earlier part of the reaction, but fell off later. In the presence of molecular oxygen, there was an apparent activation during the first ten minutes of irradiation, this being ascribed to oxidation of inhibiting substances assumed to be present in the preparations employed. No reactivation could be obtained by the addition of tryptophane or yeast gums. On the contrary, these additions, particularly the yeast gums, hasten the postinactivation which occurs on standing in preparations which have been previously irradiated for ten minutes.[128]

Recently, the activating effects of very brief irradiation (3650 and 3660A), of 5 minutes for autolyzates or half that long for dialyzates, was again noted by Gorbach with Ruess.[129] The effect is observed after the irradiated solutions have stood a short while, increasing to a maximum and then declining with time. Repeated short irradiations give greater activation than a single longer one.

[122] Kumanomidoh, S., with Pincussen, L., *Biochem. Z.*, **195**, 79 (1928).
[123] Banerjee, S., and Sen, H. K., *J. Indian Chem. Soc.*, **12**, 379 (1935); *Chem. Abs.*, **30**, 113 (1936).
[124] Huchinson, A. H., and Ashton, M. R., *Canadian J. Research*, **9**, 49 (1933); *Chem. Abs.*, **27**, 5353 (1933).
[125] Tang, T.-H., and Sung, T.-T., *J. Chinese Chem. Soc.*, **5**, 174 (1937); *Chem. Abs.*, **31**, 6405 (1937).
[126] Gorbach, G., and Lerch, K., *Biochem. Z.*, **219**, 122 (1930); *Chem. Abs.*, **24**, 2769 (1930); *Biochem. Z.*, **235**, 259 (1931); *Chem. Abs.*, **25**, 4565 (1931).
[127] Gorbach, G., and Pick, H., *Monatsh.*, **61**, 29 (1932); *Chem. Abs.*, **27**, 110 (1933).
[128] Gorbach, G., and Kimovec, D., *Monatsh.*, **61**, 39 (1932); *Chem. Abs.*, **27**, 110 (1933).
[129] Gorbach, G., with Ruess, H., *Biochem. Z.*, **271**, 338 (1934); *Chem. Abs.*, **29**, 2186 (1935); *Biochem. Z.*, **280**, 213 (1935); *Chem. Abs.*, **30**, 120 (1936).

Albers and Meyer[130] doubt the evidence of Gorbach that tryptophane is the carrier of the enzyme activity, since, although tryptophane could be detected in the purest preparations of this enzyme, its content was not proportional to the enzyme activity. The observed increase in the absorption, particularly of the longer wave-lengths, was attributed to an aggregation of the colloidal carrier accompanied by an alteration or masking of the active groups.[130a]

Ultraviolet light retards the action of phosphatase from tuberculous lymph glands of rabbits on calcium fructose mono- and sucrose-phosphate, but not on calcium α-glycerophosphate. In the presence of eosin, sunlight also diminished the activity of the phosphatase.[131] Collier and Wasteneys[132] find that plasma phosphatase may be destroyed by ultraviolet and by visible light.

Lipase. There have been recent claims that monochromatic radiations of long wave-length stimulate the activity of lipase. This effect, at least that on the action of the lipase of autolyzed yeast on castor oil, is said to be decreased when light of greater intensities is used.[133] Ultraviolet rays, however, inactivate lipase.[134] Similar observations have been recorded on the destruction of lipase in the blood serum of rabbits or guinea pigs. The proteins in the serum exert a protective action and the effects are greater when part of the protein content is removed.[135]

Irradiation of dry powdered seeds of *Ricinus communis* does not affect their lipase activity.[136]

Proteinases. That pepsin solutions can be inactivated by ultraviolet rays by a monomolecular reaction was observed by Hussey and Thompson and later confirmed by Gates.[137] Northrop[138] found the loss of activity of his crystalline preparations caused by either ultraviolet rays or radium to be exactly proportional to the rate of loss of proteins by denaturation. This was evidence supporting the view that the enzyme is a crystalline protein and not merely some simpler substance carried by the protein, or at any rate that the protein molecule is itself responsible for the enzyme activity of the preparation. The rate of inactivation varied with the pH of the solution; it had its maximum value at pH 2. Uehara places it at pH 1.4.[139]

The preparations exhibit an absorption band between 2600 and 2900A. At low temperatures this may be resolved into a number of sharp narrow bands.[140] Gates found in a series of experiments with monochromatic ultraviolet light that the destruction of pepsin by different wave-lengths agrees in general with its absorption spectrum. Thus, by plotting the reciprocals of the energies required for various wave-lengths to produce the same degree of inactivation there is obtained a curve,

[130] Albers, H., and Meyer, I., *Z. physiol. Chem.*, **228**, 122 (1934).
[130a] This, however, may be not necessarily the case since similar increases in absorption during brief irradiation periods have been observed in crystalline pepsin and uracil solutions where there is no possibility of the presence of a carrier of high molecular weight.
[131] Horii, I., *Arb. Inst. Univ. Kyoto*, III *C*, 62, 1931; *Brit. Chem. Abs.*, **A**, 874 (1932).
[132] Collier, H. B., and Wasteneys, H., *Australian J. Exp. Biol. Med. Sci.*, **9**, 89 (1932); *Chem. Abs.*, **27**, 2164 (1933).
[133] Murakami, R., *J. Agr. Chem. Soc. Japan*, **12**, 709 (1936); *Chem. Abs.*, **31**, 1436 (1937). This author made similar observations on yeast amylase, proteinase and urease, *J. Agr. Chem. Soc. Japan*, **12**, 175, 180 (1936); **12**, 151; **13**, 46 (1937).
[134] Takayama, T., *Bull. Agr. Chem. Soc. Japan*, **5**, 71 (1929); *Chem. Abs.*, **25**, 123 (1931).
[135] Pincussen, L., and Hayashi, S., *Biochem. Z.*, **195**, 196 (1928).
[136] Cousin, E., and Creach, P., *Bull. soc. pharm. Bordeaux*, **75**, 12 (1937); *Chem. Abs.*, **31**, 6681 (1937).
[137] Gates, F. L., *J. Gen. Physiol.*, **17**, 797 (1933-4); **18**, 265 (1934).
[138] Northrop, J. H., *J. Gen. Physiol.*, **17**, 359 (1934).
[139] Pincussen, L., and Uehara, K., *Biochem. Z.*, **195**, 87 (1928).
[140] Lavin, G. I., Northrop, J. H., and Taylor, H. S., *J. Am. Chem. Soc.*, **55**, 3497 (1933); **57**, 874 (1935).

the destruction spectrum, which is similar in form and location to the absorption spectrum. During the process of irradiation, an increase in absorption occurs at wave-lengths other than that of the maximum absorption. Thus the minimum in the absorption spectrum at about 2500A was gradually lost and the long wave-length leg of the absorption curve also showed a very considerable increase in absorption.[141] A protective action by proteins also has been observed in the case of this enzyme by Banerjee and Sen.[142]

Trypsin also is inactivated by ultraviolet but not by visible rays. The effect is maximal in the absence of iodides of the alkalies or alkaline earths.[143]

The eosin-sensitized photochemical destruction of rennet by visible light follows a unimolecular course, the rate constant being independent of the time of irradiation until 60 per cent of the enzyme has weakened. Its value increases with the concentration of the enzyme and is proportional to the intensity of illumination.[144]

Purified tyrosinase can be injured by irradiation, according to Pincussen and Hammerich.[145] It is suggested that this may in some manner be concerned with the formation of melanins from tyrosine or related substances in irradiated skin. Alverdes [146] believed that yellow rays promote the activity of the tyrosinase of the larvae of *Cyclops viridis*.

The destruction and absorption spectra of urease in the ultraviolet region are believed coincident by Kubowitz and Haas.[147] According to Pincussen and Kato,[148] sunlight acting on urease solutions at pH 6.4 diminished the activity both of the active constituents and of a so-called "stable Component-X." Potassium hydrogen phosphate at pH 5.6 affords partial protection to the active component, but even in darkness the activity of the other constituents is decreased by phosphate. Ultraviolet irradiation destroys the active enzyme both in the presence and absence of phosphate, but does not have such a marked effect as sunlight in inhibiting Component X. Collier and Wasteneys [149] found that impure urease may be destroyed not only by ultraviolet but also by infrared rays. The quantity of ammonia produced by soy urease is said, however, to increase with the intensity of monochromatic light of various wave-lengths tested by Murakami.[150] Crystalline urease is rapidly destroyed by ultraviolet irradiation and cannot be reactivated by reducing agents or tissue extracts. Irradiated urease produces no antiurease when injected into animals.[151]

Ultraviolet rays decrease the activity of animal rennet, although they have no effect on the rennet derived from plants, such as thistle blossoms.[152] Ultraviolet light destroys thrombin, but prothrombin is more resistant, according to Cekada.[153]

[141] Note also Collier, H. B., and Wasteneys, H., *Australian J. Exp. Biol. Med. Sci.*, **9**, 89 (1932); *Chem. Abs.*, **27**, 2164 (1933).

[142] Banerjee, S., and Sen, H. K., *J. Indian Chem. Soc.*, **12**, 740 (1935); *Chem. Abs.*, **30**, 2581 (1936).

[143] Pincussen, L., and Klissiunis, N., *Biochem. Z.*, **152**, 416 (1924); Pace, J., *Ibid.*, **240**, 490 (1931).

[144] Schmidt-Nielsen, S., and Fjermeros, E., *Compt. rend. trav. lab. Carlsberg, Sér. chim.*, **22**, 473 (1938); *Chem. Abs.*, **32**, 6266 (1938).

[145] Pincussen, L., and Hammerich, T., *Biochem. Z.*, **239**, 273 (1931).

[146] Alverdes, F., *Archiv Entwickl. Organ.*, **47**, 375 (1921).

[147] Kubowitz, F., and Haas, E., *Biochem. Z.*, **257**, 337 (1933).

[148] Pincussen, L., and Kato, N., *Biochem. Z.*, **142**, 228 (1923).

[149] Collier, H. B., and Wasteneys, H., *Australian J. Exp. Biol. Med. Sci.*, **9**, 89 (1932); *Chem. Abs.*, **27**, 2164 (1933).

[150] Murakami, R. J., *Agr. Chem. Soc. Japan*, **13**, 439 (1937); *Chem. Abs.*, **32**, 1723 (1938).

[151] Pillemer, L., Ecker, E. E., Myers, V. C., and Muntwyler, E., *J. Biol. Chem.*, **123**, 365 (1938).

[152] Christen, C., and Virasoro, E., *Lait*, **15**, 354, 496 (1935); *Chem. Abs.*, **29**, 5134 (1935).

[153] Cekada, E. B., *Am. J. Physiol.*, **78**, 512 (1926): For the behavior of baicalinase, see Miwa, T., *Acta Physicochim.*, **9**, 89 (1936); *Chem. Abs.*, **30**, 8272 (1936), and for β-glucuronosidase, Oshima, G., *J. Biochem. (Japan)*, **23**, 305 (1936); *Chem. Abs.*, **30**, 4882 (1936).

Enzymes Concerned with Respiration. Ito [154] noted that catalase has two absorption bands at 4060 and 2660A, the first corresponding to the absorption band of hemin. Quite different was the earlier statement by Kuhn, Hand and Florkin [155] that the absorption spectrum of catalase shows three bands at 6290, 5400 and 5000A, in contrast to the continuous visible absorption of peroxidase. Zeile and Hellström [156] also gave absorption spectral evidence that liver catalase contained a porphyrin iron complex, the carrier of the catalase function.

Blood catalase is more readily destroyed in dilute than in stronger solutions, and the most rapidly at pH 6.81, the optimum for its activity.[157] The addition of salts protected the catalase from the action of light. In the case of potassium iodide, the results were complicated by the action of the iodine liberated by the light. Morgulis and Schumacher [158] found that the process proceeds at a uniform rate at pH 6.28. At more acid or alkaline reactions, the initial rate of inactivation diminishes considerably with the lapse of time. At pH 11, this effect is so marked that the enzyme may be said to be actually stabilized against the radiations.

Spectrographic determinations have been used in an original manner by Stern [159] in following the formation of intermediate compounds during the action of this enzyme. He noted that purified catalase solutions show, in addition to the hematin absorption in the visible regions, ultraviolet bands due to the protein carrier. These varied with the source from which the catalase had been prepared. Irradiation from a mercury lamp inactivated the enzyme and changed its fluorescence from yellow-green to blue-green. This effect did not occur if a nickel oxide filter was interposed.

Califano [160] believed that by irradiation with blue mercury lines 4050 to 4360A, the intensity of catalase activity is decreased. There is little action by 4920A and none by 5460 and 5780A. The compound of catalase and carbon monoxide is decomposed by the 4050A line and less so by that at 4920A.

Ultraviolet irradiation of yeast cells has been claimed to increase their catalase activity several times.[161] After 16 to 18 hours it increases 300 per cent in *Saccharomyces ellipsoideus*, 1000 per cent in *Torula rosa* and 2500 per cent in *Torula colliculosa*. However, there was only a slight increase in the case of silkworm eggs.[162]

Green-colored rice may be decolorized by sunlight, but not by ultraviolet rays. During this process, the catalase and peroxidase activities decreased remarkably, but this also did not occur when ultraviolet rays were used.[163]

From absorption data, Kuhn, Hand and Florkin [164] believed it probable that the active group in peroxidase is an iron porphyrin compound. The absorption

[154] Ito, R., *J. Biochem., Japan*, **22**, 139 (1935); *Chem. Abs.*, **29**, 8025 (1935).

[155] Kuhn, R., Hand, D. B., and Florkin, M., *Z. physiol. Chem.*, **201**, 255 (1931).

[156] Zeile, K., and Hellström, H., *Z. physiol. Chem.*, **192**, 171 (1930). See also Stern, K. G., *J. Biol. Chem.*, **121**, 561 (1937).

[157] Pincussen, L., and Seligsohn, F., *Biochem. Z.*, **168**, 457 (1926).

[158] Morgulis, S., and Schumacher, L., *J. Biochem.*, **86**, 75 (1930).

[159] Stern, K. G., *Nature*, **136**, 335 (1935); **136**, 302 (1935); *Z. physiol. Chem.*, **212**, 207 (1932); **219**, 105 (1933).

[160] Califano, L., *Naturwiss.*, **22**, 249 (1934); *Chem. Abs.*, **28**, 5478 (1934).

[161] van Euler, H., and Günther, G., *Z. physiol. Chem.* **220**, 69 (1933); *Chem. Abs.*, **27**, 5343 (1933). Variations in intensity are believed more significant than variations in wave-length by Murakami, R., *J. Agr. Chem. Soc. Japan*, **13**, 429, 435 (1937); *Chem. Abs.*, **32**, 1723 (1938).

[162] Yamafuji, K., *Enzymologia*, **1**, 120 (1936); **2**, 147 (1937); *Chem. Abs.*, **30**, 7600 (1936); **32**, 9101 (1938). Similar observations on Spirogyra were recorded by Burge, W. E., and Burge, E. L., *Bot. Gaz.*, **77**, 220 (1924).

[163] Kondo, M., and Okamura, T., *J. Sci. Agr. Soc. Japan, No. 327*, 67 (1931); *Chem. Abs.*, **25**, 5689 (1931).

[164] Kuhn, R., Hand, D. B., and Florkin, M., *Z. physiol. Chem.*, **201**, 255 (1931).

appeared to be continuous and located in the visible region. Peroxidase inhibited by carbon monoxide could not be reactivated by light. According to Pincussen and Hammerich [165] this enzyme is destroyed also by the rays of the quartz mercury arc, the loss of activity being almost proportional to the light intensity. Aside from the fact that the greatest destruction occurs in acid solution, the pH has relatively little influence upon the process.

An enzyme of the liver which oxidizes ethyl alcohol is also inactivated by ultraviolet light.[166] Keilin [167] believes the indophenol oxidase system of yeast cells which has been impaired by combination with carbon monoxide may be regenerated by the dissociating action of light.

The xanthine oxidase obtainable from milk may be inactivated by sunlight, ultraviolet light or radium, according to Toyama.[168] Its absorption band has a maximum at 2790A; this is shifted toward greater wave-lengths in an alkaline medium.[169]

The action of a specific dehydrogenase in decolorizing methylene blue in the presence of alcohol as the hydrogen donor in an evacuated Thunberg tube may be accelerated by irradiation with a quartz mercury lamp.[170] According to von Euler and Klussmann,[171] this is not due to a rise in temperature, to a photochemical action on the dye alone, or to photoöxidation of the yeast extract. The effect is absent if a succino-dehydrogenase or liver extract system is used, but the effect is observed when apozymase and cozymase are used instead of yeast. von Euler, Hellström and Brandt [172] believe that the reduction of methylene blue in a dehydrase-alcohol system is accelerated by red light. A photoreduction of methylene blue likewise takes place in the absence of enzymes in the presence of alcohol as the hydrogen donor. The number of reduced dye molecules varied from one to 6000 to one to 35 quanta under various conditions with red and with ultraviolet light. At pH 5.1, the reduction is one hundred times as fast as at pH 7. The reduction is accelerated by ferrous ions. The irradiated dye fluoresces; a single band appears at 6780 to 6800A.

The dehydrogenase of beef liver represents a complex system in which, besides glucose and the enzyme itself, there are also present a coenzyme and a flavin-enzyme. Adler and von Euler [173] found that green and blue light did not affect the reaction velocity, but a red filter (675 to 645 mμ), which corresponds to the absorption maximum of methylene blue, was effective in activating the system. This means that the photoactivation occurs upon the dye. Illumination of the complete system with visible light doubles the reaction velocity. In the absence of flavin, the reaction proceeds normally if light is supplied, so that the flavin does not participate in the light activity. Inhibition by copper occurs in light or darkness and in the presence or absence of flavin, so that it must represent a direct effect upon the dehydrogenating enzyme. That cozymase is an indispensable component of the system shows it to be functionally interdependent with dehydrogenase. When a constant light intensity is used, the speed of inactivation decreases with

[165] Pincussen, L., and Hammerich, T., *Biochem. Z.*, **241**, 384 (1931).
[166] Mizusawa, H., *J. Biochem. Japan*, **18**, 243 (1933); *Chem. Abs.*, **28**, 794 (1934).
[167] Keilin, D., *Nature*, **119**, 670 (1927).
[168] Toyama, J., *Fukuoka-Ikwadai Gaku-Zasshi*, **26**, 1483 (1933); *Chem. Abs.*, **28**, 7279 (1936).
[169] Ito, R., *J. Biochem. Japan*, **22**, 139 (1935); *Chem. Abs.*, **29**, 8025 (1935).
[170] Krestownikoff, A. N., *Skand. Arch. Physiol.*, **52**, 199 (1927); *Brit. Chem. Abs.*, **A**, 445 (1928).
[171] von Euler, H., and Klussmann, E., *Naturwiss.*, **22**, 777 (1934); von Euler, H., *Arkiv Kemi, Mineral Geol.*, **11B**, 45 (1934).
[172] von Euler, H., Hellström, H., and Brandt, K., *Naturwiss.*, **23**, 486 (1935).
[173] Adler, E., and von Euler, H., *Z. physiol. Chem.*, **232**, 6, 10, 16 (1935).

increasing cozymase concentration.[174] Cozymase differs from the coenzyme of the Warburg dehydrogenase in that the former but not the latter can be destroyed in solutions as concentrated as one mg. per cc.

Junghagen [175] finds the dehydrogenases of pyruvic and glycerophosphoric acids to be rapidly destroyed by ultraviolet light. In the range between pH 6 and 8, succinodehydrogenase is also injured by ultraviolet light, but the destruction is not so rapid in acid solutions.[176] Exposure to ordinary light for an hour also causes injury, but exposure for only half an hour merely stimulates the activity of the enzyme.

Warburg [177] made extensive use of irradiation and spectrographic methods in his investigations of his new hemin-containing respiratory enzyme.

He found its compound with carbon monoxide to be dissociable by light; and, by quantitative determinations of the intensities of various wave-lengths required to produce a given amount of destruction, determined the absorption spectrum of the carbon monoxide compound of the enzyme.[178] Irradiation of yeast cells with equal intensities of monochromatic light of various wave-lengths caused an increase in the rate of respiration of the cells. By plotting this effect against the wave-lengths, he obtained a curve of the absorption of light by the hemin of the enzyme. The spectrum of the respiratory enzyme so obtained is similar in shape to the absorption curve of the carbon monoxide compound of reduced hemin. The maximum of the latter curve is, however, at 408 mμ, and that of the respiratory enzyme is at 436 mμ. This discrepancy is accounted for by the assumption that the respiratory enzyme exists in the solid state adsorbed on the surface of the cells.

In the course of these investigations the absorption spectra of carbon monoxide, iron carbonyl, pyridine-hemin, and the compound of carbon monoxide and ferrocysteine were examined. These comparative absorption spectra show not merely that the iron carbonyl group is a part of the respiratory enzyme but also that it is attached to a hemin-like molecule. The absorption curve for the carbon monoxide-ferrocysteine compound is quite different.[179] Warburg, Negelein and Christian [180] found carbon monoxide-hemoglobin in carbylamine solutions to be the most light-sensitive carbon monoxide-iron-porphyrin compound then known.

In tissue sections, a blue fluorescence in Wood's light due to proteins gives way on continued irradiation to a red fluorescence characteristic of free porphyrin liberated from any complexes present by photolysis.[181]

A respiratory enzyme derived from the retina has an absorption spectrum identical with that of the enzyme derived from yeast.[182] The respiratory enzyme differs from cytochrome. A new yellow oxidation enzyme is also obtainable from bottom yeast.[183] Its absorption spectrum has three bands, two of which, at 465 and 495 mμ, are in the long wave-length range.[184] The enzyme has an active group, a reversible yellow pigment, bound to a colloidal protein carrier. The active group can be split from the protein by aqueous methanol. It fluoresces green and is catalytically inactive, but the light absorption in the visible range is almost unchanged. It has two bands in the ultraviolet at 2700 and 3500A, and also one at 4450A.[185] When irradiated in dilute alkaline solution,

[174] von Euler, H., and Schlenk, *Arkiv Kemi, Mineral Geol.*, **12B**, No. 19 (1936).
[175] Junghagen, S., *Skand. Arch. Physiol.*, **54**, 115 (1928); *Chem. Abs.*, **22**, 4549 (1928).
[176] Pincussen, L., and Roman, W., *Biochem. Z.*, **229**, 281 (1930).
[177] Warburg, O., *Naturwiss.*, **16**, 345 (1928); Warburg, O., and Negelein, E., *Naturwiss.*, **16**, 856 (1928); *Biochem. Z.*, **202**, 202 (1928).
[178] Warburg, O., and Negelein, E., *Biochem. Z.*, **214**, 64 (1929).
[179] *Cf.* also Cremer, W., *Biochem. Z.*, **194**, 231 (1928); Krebs, H. A., *Ibid.*, **193**, 347 (1928). For the splitting by light of the carbon monoxide-ferroglutathione compound, see Kubowitz, F., *Biochem. Z.*, **282**, 277 (1934).
[180] Warburg, O., Negelein, E., and Christian, W., *Biochem. Z*, **214**, 26 (1929).
[181] Thomas, J., *Compt. rend. soc. biol.*, **125**, 386 (1937); *Chem. Abs.*, **31**, 6681 (1937).
[182] Warburg, O., and Negelein, E., *Biochem. Z.*, **214**, 101 (1929).
[183] Warburg, O., and Christian, W., *Biochem. Z.*, **254**, 438 (1932).
[184] Warburg, O., and Christian, W., *Naturwiss.*, **20**, 980 (1932); Kubowitz, F., and Haas, E., *Biochem. Z.*, **255**, 247 (1932).
[185] *Biochem. Z.*, **258**, 496 (1933); **263**, 228 (1933); **266**, 377 (1933).

the active component, after acidification, becomes soluble in chloroform. It yields a crystalline derivative, $C_{13}H_{12}N_4O_2$, from which it is possible to obtain urea and a compound, $C_9H_{10}N_2O_2$.[186] Theorell [187] has recently found the yellow coenzyme portion obtained after separation from the protein to consist of a flavine esterified with phosphoric acid and therefore related to the vitamin B_2 of the German workers.[187a]

Bénard, Biancani, and Biancani [188] observed that ultraviolet light dissociates the compound of carbon monoxide with hemoglobin.

Warburg and Christian [189] find that the irradiation of one microgram of their hydrogen-transferring coenzyme in 1 cc. of water with a quartz lamp destroys its catalytic activity in fifteen minutes. In a glass tube or with a solution a thousand times as concentrated, there is no measurable destruction in this time. The time required for the half destruction by an intensity of one calorie per square meter per minute (calculated from data obtained at other intensities) increases with the wave-length. It is 520 times as large at 2830A as at 1860A. From an analysis of the data, the conclusion is drawn that not all of the light absorbed, but only that absorbed by a special group in the coenzyme, brings about its destruction.

The work on the relation of ultraviolet light to the respiratory enzymes has been extensively reviewed by Wynd and Reynolds.[190]

Hormones [191]

Künster [192] claims that the actions of various plant hormones are materially affected by irradiation.

The effects of ultraviolet light on insulin have been discussed in connection with the proteins. Adrenaline, according to Keeser,[193] is activated by red and green light and inhibited by blue light. Pennetti [194] states that, in the presence of eosin, adrenalin may be inactivated by sunlight. Some protective power is exerted against this action by pyrogallol, hydroquinone and resorcinol, but not by gelatin, egg albumin, Witte's peptone or glucose. Absorption data for adrenaline and ephedrine have been given by Marchlewski and Skarzynski,[195] who find that the stereoisomers of these products have identical absorption spectra.

The rate of oxidation of commercial adrenaline solutions with hydrogen peroxide and in light is independent of the pH, but in pure solutions of the hydrochloride an increase in rate with increase in pH can be observed. The intensity of the photoöxidation depends on the intensity and wave-lengths of the light employed; irradiation with ultraviolet light alone is said to cause less change than when both visible and invisible rays are used.[196]

Ephedrine solutions are unstable in sunlight, benzalephedrine being one of the

[186] See also Warburg, O., and Haas, E., *Naturwiss.*, **22**, 20 (1934).

[187] Theorell, H., *Biochem. Z.*, **278**, 263 (1935).

[187a] (See Chapter 42.)

[188] Bénard, H., Biancani, E., and Biancani, H., *Compt. rend. soc. biol.*, **92**, 1031 (1925); *Chem. Abs.*, **19**, 3278 (1925).

[189] Warburg, O., and Christian, W., *Biochem. Z.*, **282**, 221 (1935).

[190] Wynd, F. L., and Reynolds, E. S., *Ann. Mo. Botan. Gardens*, **22**, 771 (1935).

[191] It has been proposed to treat glands of internal secretion with ultraviolet light in order to render them or their extracts increasingly active. Eichelbaum G., and Altenburg, J., British P. 275,183, June 21, 1927; *Brit. Chem. Abs.*, **B**, 874 (1928).

[192] Küstner, H., *Deut. Med. Wochschr.*, **58**, 625 (1932); *Chem. Abs.*, **26**, 4831 (1932).

[193] Keeser, E., *Arch. exp. Path. Pharmakol.*, **166**, 624 (1932).

[194] Pennetti, G., *Arch. sci. biol.*, **9**, 398 (1927); *Chem. Abs.*, **21**, 3678 (1927).

[195] Marchlewski, L., and Skarzynski, B., *Bull. intern. acad. Polonaise*, **A**, 241 (1929); *Chem. Abs.*, **24**, 873 (1930).

[196] Vacek, T., *Compt. rend. soc. biol.*, **109**, 583 (1929); *Chem. Abs.*, **25**, 1330 (1931).

[197] Moore, E. E., and Moore, M. B., *Ind. Eng. Chem.*, **23**, 21 (1931).

chief decomposition products.[197] It was claimed by Terata and Ito [198] that adrenalin gains in potency (depression of intestinal motility, stimulation of uterus and vasoconstrictor action) after ultraviolet irradiation or after artificial light treatment. Ten "sunlight units," however, decreased its action. Verda, Kneer and Burge [199] find 1 : 15,000 solutions to lose their pressor effect after quartz lamp treatment. Haddock [200] states that the effects are not marked and involve mainly racemization and slight oxidation. Ewing [201] finds the physiological activity of adrenalin solutions to be completely destroyed by exposure to ultraviolet light. The decomposition products, which have no pressor action, are similar to those formed by the action of hydrogen peroxide. The activity of solutions of synephrine salts and of *p*-hydroxyphenylpropanolamine is markedly increased by moderate, but destroyed by excessive, irradiation. The activity of solutions of synephrine base is not changed by irradiation.[202]

Prolan is inactivated by ultraviolet rays. Zondek and von Euler [203] believed the thermal stability so similar to the ultraviolet stability as to support the view that prolan is a catalyst of enzymic nature. The absorption maximum for follicular hormones lies at 2800 to 2850A.[204] Concentrates of the oxytocic hormone of the pituitary glands are inactivated by ultraviolet rays.[205] The same is true of the hormones of the ovarian follicles and placenta, the destruction probably being by oxidation.[206]

The Schering-Kahlbaum Co.[207] propose the ultraviolet irradiation of extracts of germinal gland hormones.

When human thyroid gland pulp is subjected to ultraviolet irradiation, iodine ions separate to the extent of 0.5 to 2.7 per cent of the total iodine content.[208] Westra and Hunter[209] exposed finely hashed non-goitrogenic cabbage in thin layers at 50 cm. from a mercury-vapor lamp for thirty to 120 minutes. Rabbits fed exclusively on this cabbage for twelve weeks did not develop goitre.

Secretin is quickly inactivated by ultraviolet irradiation. The absorption of ultraviolet light is thereby increased, probably because of the absorption of aldehydes formed by an extensive decomposition of the molecule. All the nitrogen is freed as ammonia.[210] Although secretin is destroyed, the villikinin in extracts from the intestinal mucosa is not; this favors the independent nature of these substances.[211]

[198] Terata, B., and Ito, R., *Folia Pharmacol. Japon.*, **12**, No. 1, 74; No. 2, 125 (1931); *Chem. Abs.*, **25**, 3127, 5708 (1931); *Manshu Igaku Zasshi*, **26**, 619, 863 (1937); *Chem. Abs.*, **32**, 8453 (1938).

[199] Verda, D. J., Kneer, L., and Burge, W. E., *J. Pharmacol.*, **42**, 383 (1931); *Chem. Abs.*, **25**, 5935 (1931). See also Ewing, P. L., Blickensdorfer, P., and McGuigan, H., *J. Pharmacol.*, **43**, 125 (1931); *Chem. Abs.*, **26**, 1004 (1932).

[200] Haddock, L. A., *Quart. J. Pharm. Pharmacol.*, **6**, 496 (1933); *Chem. Abs.*, **28**, 1137 (1936).

[201] Ewing, P. L., *J. Lab. Clin. Med.*, **20**, 16 (1934); *Chem. Abs.*, **29**, 2233 (1935).

[202] See also Higgins, J. A., Ewing, P. L., and McGuigan, H. A., *J. Pharmacol.*, **44**, 353 (1932); *Chem. Abs.*, **26**, 3302 (1932).

[203] Zondek, B., and von Euler, H., *Skand. Arch. Physiol.*, **68**, 232 (1934); *Chem. Abs.*, **28**, 4085 (1934).

[204] Slotta, K. H., Ruschig, H., and Fels, E., *Ber.*, **67B**, 1270 (1934); Fernholz, E., *Ibid.*, 1855; Butenandt, A., and Schmidt, J., *Ibid.*, 2088; von Euler, H., and Brandt, K., *Arkiv Kemi, Mineral. Geol.*, **11B**, 51 (1935); *Naturwiss.*, **23**, 544 (1935); Chevallier, A., Cornil, L., and Verdollin, J., *Bull. Acad. Med.*, **114**, 171 (1935); *Chem. Abs.*, **29**, 8088 (1935). Bugyi, B., *Z. ges. exptl. Med.*, **101**, 14 (1937).

[205] Das, N., and Guha, B. C., *Indian J. Med. Research*, **21**, 765 (1934); *Chem. Abs.*, **29**, 1150 (1935).

[206] Allen, E., and Ellis, M. M., *J. Am. Med. Assoc.*, **85**, 94 (1925).

[207] British P. 295,361, Aug. 8, 1927, to Schering-Kahlbaum Co.; *Brit. Chem. Abs.*, **B**, 37 (1930).

[208] Lieben, F., and Kraus, H., *Biochem. Z.*, **236**, 182 (1931).

[209] Westra, J. J., and Hunter, V., *Proc. Soc. Exp. Biol. Med.*, **30**, 1157 (1933); *Chem. Abs.*, **28**, 814 (1934).

[210] Ågren, G., *Skand. Arch. Physiol.*, **70**, 10 (1934); *Chem. Abs.*, **29**, 1475 (1935).

[211] Ludany, G., *Biochem. Z.*, **285**, 192 (1936).

Irradiation of an alkaline extract of the pigment hormone of the posterior lobe of the hypophysis does not affect its ability to cause on injection a temperature decrease and a blood sugar increase.[212]

Products of Pathological Significance

The toxin, ricin, could not be destroyed by ultraviolet light of wave-lengths 2250 to 2540A in experiments by Carmichael.[213]

Irradiation of tetanus toxin destroys its toxic but not its antigenic powers.[214] The toxicity of diphtheria toxin is also destroyed.[215] Irradiation for 48 hours causes a marked change in the absorption curve.[216]

Tuberculin. High dilutions of tuberculin are markedly inactivated by intense exposures to the quartz lamp.[217] The inactivity of light of short wave-lengths on concentrated "old tuberculin" was considered to be due to the lack of penetration of these rays. In weaker solutions, the activity on intracutaneous injection is diminished but the general reacting power is retained. The therapeutic use of light-treated tuberculin is recommended therefore as obviating the painful cutaneous reactions. This preparation is called ultratuberculin.

After irradiation, the "old tuberculin" solutions were incapable of causing intracutaneous reactions in tuberculosis guinea pigs and in suitable doses did not kill tuberculous guinea pigs.[218] This is in distinction to the results obtained in man, where rayed tuberculin produced both focal and general reactions. This difference is explained by assuming either that unchanged tuberculin is still present after irradiation or that the reactions in man are of a non-specific nature.

During irradiation of tuberculin, the pH of the solutions shifted toward the acid side and the surface tension increased, according to Mikhailovski.[219] Spiegel-Adolf and Seibert [220] measured the ultraviolet absorption spectra of highly purified tuberculin preparations made from various organisms. Considerable variations in absorption were observed. All preparations made from human type bacilli by precipitation with trichloroacetic acid contained a substance showing selective absorption with a maximum at 2650 to 2670A, spectrographically identical with nucleic acid. Nevertheless, the content of nucleic acid as measured by the absorption band could not be correlated with the biological activity of the preparations, since some in which the absorption band was missing were still biologically active. When preparations in 0.1-per cent and 1-per cent concentrations were irradiated in a quartz-covered dish for six to ten hours at 15 cm. from a quartz mercury arc, the absorption band disappeared and the toxicity, as measured by the intradermal test and the lethal action on tuberculous guinea pigs, was lost. Thus, although nucleic acid does not appear to be identical with the potent principle of tuberculin, there seems nevertheless some sort of association between it and the potent principle.

[212] Jores, A., *Z. ges. exptl. Med.*, **97**, 207 (1935).

[213] Carmichael, E. B., *J. Pharmacol. Exp. Therap.*, **35**, 193 (1929).

[214] Megrail, E., and Welch, H., *Proc. Soc. Biol. Med.*, **28**, 494 (1931).

[215] Nakayama, Y., *Japan. J. Mikrobiol. Path.*, **27**, 990 (1933); *Chem. Abs.*, **27**, 4581 (1933); Lowenstein, *Vienna Z. Path. Therap.*, **15**, 279 (1914); *Chem. Abs.*, **9**, 653 (1915).

[216] Levaditi, C., Loiseau, G., Paic, M., Philippe, M., and Haber, P., *Compt. rend. soc. biol.*, **116**, 609 (1934); *Chem. Abs.*, **28**, 5846 (1934). For further absorption data, see Ottensooser, F., Krupski, A., and Almasy, F., *Biochem. Z.*, **277**, 314 (1935) and Wadsworth, A., Crowe, M. O'L., and Smith, L. A., *Brit. J. Exptl. Path.*, **16**, 201 (1935). From the absorption data, the presence of a hemochromogen is indicated.

[217] Hausmann, W., Neumann, W., and Schuberth, K., *Z. Tuberk.*, **46**, 32 (1926); *Chem. Abs.*, **21**, 3678 (1927); *Z. Tuberk.*, **47**, 113 (1927); *Chem. Abs.*, **22**, 985 (1928).

[218] Fischer, A., and Hausmann, W., *Z. Tuberk.*, **58**, 328 (1930); *Chem. Abs.*, **26**, 511 (1932).

[219] Mikhailovski, S. M., *Zhur. Exp. Biol. Med.*, **9**, 12 (1928); *Chem. Abs.*, **22**, 2760 (1928).

[220] Spiegel-Adolf, M., and Seibert, F. B., *J. Biol. Chem.*, **106**, 373 (1934).

The action of cobra venom on red blood cells is completely destroyed by irradiating it in a dilution of 1 to 2000 in quartz with 72 times an erythema dose of the radiations from a mercury arc at a distance of half a meter.[221] At the same time the toxicity of the venom toward white mice was destroyed or greatly reduced. The possibility of using such attenuated venom in prophylactic treatments is suggested.

Arthus and Collins [222] found also that the toxins of *Crotalus terrificus, Lachesis lanceolatus, Vipera Russellii,* and *Naja tripudians* are decomposed by ultraviolet irradiation. The ability of cobra venom to inhibit coagulation was sometimes so changed as to cause a slight acceleration of coagulation. Snake venom could be protected from the effects of irradiation by egg-white, horse serum or Witte's peptone. Anticobra, antidaboia and antibothrops sera were little affected by irradiation unless diluted. Arthus [223] later stated that in the presence of gelatin, the effect of the treatment was to destroy both the toxicity and the antigenic power of cobra venom. Macht and Davis [224] also found ultraviolet rays to produce a rapid decrease in the potency of snake venom.

Serum "kallicrein" bound by gland activator is destroyed by ultraviolet light, the rate being largely independent of the pH.[225]

The flocculation characteristics of diphtheria toxoid are not changed after two to three hours of exposure to unfiltered mercury arc radiations, but the flocculating ability of the toxins decreased gradually. Their toxicity decreased about 30 per cent. The antiserums lost their flocculating power and not more than 30 per cent of their antitoxic power, although their behavior as regards precipitation by sodium sulfate was not affected.[226]

[221] Much, Peemöller and Haim, *Münch. Med. Wochschr.*, **74**, 1365; *Chem. Abs.*, **22**, 4641 (1928).

[222] Arthus, M., and Collins, H., *Arch. Intern. Physiol.*, **30**, 250 (1928); *Chem. Abs.*, **24**, 2172 (1930); *Brit. Chem. Abs.*, **A**, 1024 (1929).

[223] Arthus, M., *Compt. rend. soc. biol.*, **103**, 130 (1930); *Chem. Abs.*, **25**, 135 (1931).

[224] Macht, D. I., and Davis, M. E., *Proc. Soc. Exptl. Biol. Med.*, **30**, 990 (1933); note also Fulchignoni, E., *Boll. soc. ital. biol. sper.*, **11**, 429 (1936); Kopaczewski, W., *Compt. rend. soc. biol.*, **80**, 884 (1917).

[225] Werle, E., *Biochem. Z.*, **287**, 235 (1936); *Chem. Abs.*, **31**, 149 (1931).

[226] Modern, F., *Rev. inst. bacteriol. dept. nacl. hig. (Buenos Aires)*, **7**, 618 (1936); *Chem. Abs.*, **31**, 2622 (1931).

Chapter 35

The Lethal Action of Ultraviolet Rays and Sterilization

It has been known for over a half a century that ultraviolet rays are capable of killing bacteria and molds, but it is only in comparatively recent times that attempts have been made to utilize these results for the practical sterilization of foods, drugs, water and air. The method has, however, definite limitations and at present its use is becoming more and more restricted to surface sterilization of foods, the treatment of relatively expensive materials such as certain pharmaceutical preparations and the irradiation of air in operating rooms and hospital corridors. Studies of the mechanism of the lethal action are important in that they offer a method of attack on some unsolved problems of physiology and pathology.

Early History

As early as 1877, Downes and Blunt[1] discovered the bactericidal action of light on a mixture of organisms encountered in putrefying substances. They showed that rays of short wave-lengths are responsible for the lethal effects, and that these rays are capable of sterilizing either moist or dry organisms. They ascribed the action to a direct effect upon the organisms rather than to effects upon the surrounding media. They were in error, however, in concluding that the presence of oxygen is essential for bactericidal action. This error persisted a long time, being repeated and emphasized by Roux in 1887,[2] until it was corrected by Ward in 1892.[3] Studies were made of the effect of irradiation upon a number of microörganisms by Arloing[4] and by Duclaux (1885). Ward showed that, although some bactericidal action is exerted by the visible spectrum upon the anthrax bacillus, the most intense lethal effects are due to the ultraviolet rays which fail to penetrate glass. Ward suggested that the carbon arc might be used for the disinfection of small enclosed spaces, such as railway cars.

Other workers added a number of features of physical interest. Such features as the applicability of the inverse square law for the falling off of the intensity of the source with respect to distance, the comparative efficacy of intermittent and continuous irradiation, the effects of temperature and the like, attracted the attention of many workers, particularly of Henri and his collaborators. The general outcome of this work was the realization that physical or photochemical changes were involved which were in some manner dependent upon the absorption of the effective radiations by the organisms.

Ambitious attempts to replace the rather qualitative generalizations of their predecessors by a more quantitative statement of data were made by Bie and Bang in Finsen's laboratory. Each of these observers measured and recorded the energies to which the organisms were subjected in their experiments. Although their work was largely confined to the visible spectrum, it indicated that the bactericidal effect increases sharply as the wave-lengths employed are decreased. Only by the use of long exposures was any germicidal effect obtained by the use of light of the middle range of the visible spectrum. The most valuable contribution of Bie was the introduction of the use of liquid absorption filters to isolate particular spectral regions.

Bang improved the technique by eliminating the heating infrared rays, and extended the measurements into the ultraviolet by the use of quartz. A hanging drop of the

[1] Downes, A., and Blunt, T. P., *Proc. Roy. Soc.*, **26**, 488 (1877).
[2] Roux, E., *Ann. Inst. Pasteur*, **1**, 445 (1887).
[3] Ward, H. M., *Proc. Roy. Soc.*, **52**, 393 (1893); **53**, 23 (1893); **54**, 472 (1893).
[4] Arloing, S., *Compt. rend.*, **100**, 378 (1885); **101**, 511 (1886).

bacterial suspension on the lower surface of a quartz plate was exposed to radiations passing through the quartz. The plate formed the lid of a small quartz chamber, the temperature of which was maintained constant by a thermostatically controlled water jacket. Some of the observations indicated not only that the killing may be very rapid when ultraviolet light is employed, but also that the age of the organism and the temperature at which the irradiation is conducted exert an influence on the results. For example, at 30°C., a culture of *B. prodigiosus* three hours old was killed in 60 seconds, but a culture ten to fifteen hours old required 210 seconds. At 45°C., a three-hour culture was killed in fifteen seconds. This indicated that the reaction underlying the lethal mechanism possesses a positive temperature coefficient.[5]

Bang[6] also presented a curve for the relative effectiveness of various wave-lengths, consideration of which is reserved for a later section.

In 1903, Bernard and Morgan, working in MacFayden's laboratory at the Lister Institute, made a series of experiments which indicated that[7] the bactericidal action is practically confined to the region between 3290 and 2265A. By means of a quartz spectrograph, the spectrum of a carbon arc was thrown upon an agar plate superficially inoculated with a culture of *B. coli communis*. After a definite time the plate was incubated. Only that part of the surface which had been exposed to the rays from 3287 to 2265A showed any sign of bactericidal action. Later workers refining on the technique have fixed these limits somewhat differently. Bernard and Morgan found also that the cadmium and the iron arcs were more efficient than the carbon arc.

The active rays were completely arrested by thin films of agar media. The reader is reminded that an agar medium is not a simple gel of agar agar, but contains added proteins and sometimes sugar. These added foodstuffs exert a considerable filtering action. Similar results with a thin membrane of human epidermis stretched as a filter showed that it could not be hoped to sterilize pathogenic organisms located beneath the surface of the skin.

Bactericidal Spectral Regions According to Earlier Observers

The majority of workers have found the region of bactericidal activity to lie between the wave-lengths 2960 and 2100A. Thus Newcomber,[8] working with the bacillus of typhoid fever, gives the effective limits as 2800 to 2100A with no action at 2970A. Browning and Russ, using agar[9] surface cultures, a tungsten lamp, and a quartz spectrometer, reported 2960 to 2900A as bactericidal rays, with a maximum action at 2800 to 2540A. Cernovodeanu and Henri,[10] using a Cooper-Hewitt lamp and bacterial emulsions, found a maximum at about 2800A; Mashimo,[11] using agar surface cultures and a quartz spectrometer, found the bactericidal range to be from 2950 to 1860A with a maximum at 2750A. Bayne-Jones and von der Lingen[12] give 3500 to 1856A. Bang,[13] using a carbon arc at 30 amperes, found the maximum action to be produced by the wave-length 2500A.

The differences reported may be caused by variations in technique, especially the following: surface cultures can be killed by rays of less penetration, that is, of longer wave-length, than are needed for emulsions. This effect is reversed when the emulsion is agitated during irradiation. Arcs between different electrodes vary in their spectral energy distributions. Temperature and hydrogen ion concentration may affect the results.

[5] See also Thiele, H., and Wolf, K., *Arch. Hyg.*, **60**, 29; *Chem. Abs.*, **1**, 1029, (1907). Contra: Cernovodeanu, P., and Henri, V., *Compt. rend.*, **150**, 52, 549 (1910).
[6] Bang, S., *Mitteilungen aus Finsen's Medisins Lysinstitut*, **9**, 164 (1905).
[7] Bernard, J. E., and Morgan, H., *Brit. Med. J., Nov.* 14, 1903; *Proc. Roy. Soc.*, **72**, 126 (1903).
[8] Newcomber, H. S., *J. Exp. Med.*, **26**, 841 (1917).
[9] Browning, C. H., and Russ, S., *Proc. Roy. Soc.*, **110**, 33 (1917).
[10] Cernovodeanu, P., and Henri, V., *Compt. rend.*, **150**, 52 (1910).
[11] Mashimo, T., *Mem. Coll. Sci. Kyoto*, **4**, 1 (1919); *J. Sci.*, 161A (1921); *Chem. Abs.*, **15**, 1146 (1921).
[12] Bayne-Jones, S., and von der Lingen, J. S., *Bull. Johns Hopkins Hosp.*, **34**, 11 (1923); *cf.* Bovie, W. T., *Bot. Gaz.*, **61**, 1 (1916).
[13] Bang, S., cited by Henri, V., *Compt. rend.*, **155**, 315 (1912).

On the other hand Bazzoni [14] reported that the full radiation from light sources emitting wave-lengths shorter than 2500A will kill bacteria, but that isolated radiations between the limits of 2500 and 2800A will not affect bacteria in a drop of water in an exposure of an hour. He states further that several hours' exposure is needed to kill bacteria with rays of wave-lengths between 2200 and 2250A. even when their intensity is the same as that of the rapidly destructive total radiation of the same source. These findings are in contradiction with those of many subsequent workers who found bactericidal action even in narrow bands sharply isolated by a quartz spectrometer.

Since little was known regarding the distribution of intensities in the lines of the tungsten arc employed by Browning and Russ, Burger [15] repeated the experiment, using a mercury arc as the light source, and was able to demonstrate some correlation between the intensities of the lines within the lethal region and their relative killing effects.

In order to determine the practicability of exposing fruit to ultraviolet rays in order to destroy mold spores, Coblentz and Fulton at the Bureau of Standards conducted an investigation of the effects of various wave-length regions upon cultures of *Staphylococcus aureus*. In commenting upon the culture spectrogram of Brown- and Russ (see Figure 132), they stated that the sharp termination of the germicidal action in the short wave-length region may have been due to absorption of these rays in the instrument employed.

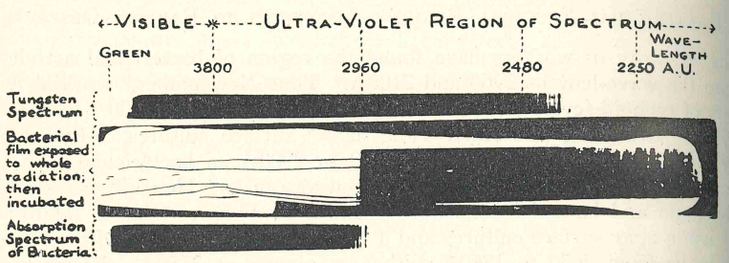


FIGURE 132. Plate of Bacteria Exposed by Spectrograph by Browning and Russ.

Coblentz and Fulton were unable to detect any effect on growth produced by irradiating agar before seeding it with the cultures, unless very high light intensities were used. The absorption spectrum of the bacterial emulsion extended from 2960 to 2100A and coincided with the spectral range of germicidal action. Slight differences in the wave-lengths effective for killing different organisms were found. Thus for *B. coli,* the range for lethal effects extended from 2960 to 2200A and for *B. typhosus* from 3000 to 2100A, and for *Staphylococcus aureus* the range of greatest germicidal action extended from 2960 to 2380A. It may be noted that in the experiments of Baynes-Jones and van der Lingen in which the long wave-length threshold was found at 3500A, the cultures were exposed to the sun for three hours. Coblentz and Fulton employed a series of mica screens of various thicknesses for isolating particular regions, the mica having a maximum absorption near 2600A. They found germicidal action even at 3650A, but very prolonged exposures were required when wave-lengths between 2970 and 3650A were used.

[14] Bazzoni, C. B., *Am. J. Public Health,* **4,** 975 (1914).
[15] Burger, G., *Bull. Basic Sci. Research,* **2,** 46 (1928).

The lethal action of rays shorter than 2800A was at least ten times more rapid than that of those longer than 3050A, in spite of the much lower intensity of the shorter rays. Intermittent exposure had the same effect as continuous exposure for the same total time of exposure, that is, the action is cumulative. These authors estimated the energy between 1700 and 2800A required to kill a single bacterium to be of the order of 19×10^{-12} watt.[16]

INTERPRETATIONS OF THE LETHAL MECHANISM

Bedford [17] attempted to revive an earlier theory of an indirect lethal mechanism in which it was assumed that the organisms are killed by the action of hydrogen peroxide formed by the ultraviolet rays. Such a mechanism would require a wave-length dependence similar to that for the production of hydrogen peroxide, which differs from the results described in the preceding paragraphs. Furthermore, such a mechanism is inadequate to account for the observed facts (described in a subsequent paragraph) regarding the relative efficiencies of various wave-lengths operating at the same intensity. Moore and Webster [18] attributed the germicidal power of sunlight to the production of formaldehyde.

Proks [19] claimed that irradiation of the culture medium previous to inoculation lessens its ability to support growth. It may be recalled that Coblentz and Fulton had observed a similar result after prolonged irradiation of agar. Blank and Arnold [20] state that radiations of 2537A change agar or agar-water gels so that they no longer support the growth of *B. subtilis.* There is formed a nonvolatile, thermostable material capable of diffusing through the gel. A similar inhibiting effect results from the addition to the medium of an irradiated solution of a carbohydrate. In confirming these results, Baumgartner [21] notes that irradiation of carbohydrates is accompanied by a marked production of acid, approximately half of which is formic. Neutralization restores the ability of the medium to support growth. Further confirmation is reported by Pratt.[22] Calabek [23] believed that the Höhensonne lamp, as well as natural solar rays, lowers the swelling capacity of agar disks to an extent dependent upon the time of irradiation. The maximum decrease was achieved after an illumination of 146 minutes on one side of the disk, the subsequent swelling in water reaching only 1525 per cent instead of the normal 3200 per cent. The action of the radiations was practically limited to the extreme layers of the gel, decreasing to about zero at 0.08 mm. below the surface. Kersten and Dwight [24] find that irradiation of dry agar decreases the viscosity and pH of the sol subsequently made.

Such effects on the medium have, however, little to do with the mechanism by which organisms on the surface of a plate are killed within a few seconds of exposure to ultraviolet rays. In this case, it is necessary to seek for a direct action of the rays upon the organisms. To determine which of the chemical constituents of the organisms absorb the light in the primary process, subsequent

[16] Coblentz, W. W., and Fulton, H. R., *Bureau of Standards Sci. Papers,* **19,** 495, 641 (1924).
[17] Bedford, T. H., *Brit. J. Exptl. Path.,* **8,** 437 (1927).
[18] Moore, B., and Webster, T. A., *Proc. Roy. Soc.,* **90,** 168 (1918).
[19] Proks, J., *Lait,* **13,** 331 (1933); *Chem. Abs.,* **27,** 3233 (1933). To eliminate effects on the media, D. G. Sharp atomizes broth cultures into air where they may be irradiated. *J. Bact.,* **35,** 589 (1938).
[20] Blank, I. H., and Arnold, W., *J. Bact.,* **30,** 507 (1935).
[21] Baumgartner, J. G., *J. Bact.,* **32,** 75 (1936).
[22] Pratt, E. L., *J. Bact.,* **32,** 613 (1936).
[23] Calabek, J., *Protoplasma,* **3,** 17 (1927); *Chem. Abs.,* **22,** 3896 (1928).
[24] Kersten, H. J., and Dwight, C. H., *J. Phys. Chem.,* **41,** 687 (1937).

workers have compared the absorption spectra of various cellular components with the spectral regions of greatest lethal activity.[25]

Following a suggestion of Henri [26] that the abiotic power of various wave-lengths parallels their absorption by proteins, Harris and Hoyt [27] found that *B. subtilis,* irradiated by ultraviolet filtered through a 1-per cent tyrosine solution, survived exposures of forty minutes. On direct exposure, the organisms were killed in 150 seconds. Similar results were obtained with *Staphylococcus aureus* and *B. mucosus capsulatus.* These experiments do not, however, afford proof that the lethal action of ultraviolet rays is to be attributed to an effect upon the aromatic amino- acids of the proteins. This work had a considerable influence on the opinions of biologists and for a time the effects of radiations upon the proteins were perhaps overemphasized.

In 1914, Henri stated [28] that the abiotic power of ultraviolet light was the result of photochemical action on certain molecular groupings of the protoplasm and, especially, the cell nucleus. In 1916, Galeotti [29] showed that the reproductivity of *B. typhosus, B. paratyphosis* and *B. subtilis* could be destroyed by less intense ultraviolet light without causing them to lose their motility, an indication that the first locus of attack is upon some material associated with cell division. Bovie and Hughes [30] found that exposures of *Paramecium caudatum* only one-thirteenth as long as those necessary to produce cytolysis were sufficient to inhibit all division.

Some observers have described changes wrought in bacteria by non-sterilizing doses of ultraviolet rays. Henri [31] claimed to have produced two new forms from anthrax bacilli in this manner. Eberson [32] believed the irradiation of certain types of mengingoccoci to diminish their virulence and increase their antigenic power. However, attention has not been devoted to any extent to this type of ultraviolet effect.

In 1928, Gates published a brief note stating that [33] "the reciprocal of the bactericidal energy curves matches the absorption curves for certain of the nucleoproteins—cytosine, thymine and uracil—more closely than it does those for various aromatic acids such as tyrosine, tryptophane and phenylalanine, suggested by Harris and Hoyt." That derivatives of the nucleic acids should be concerned agrees well with the observations that it is the reproductive function which is first destroyed by the action of ultraviolet rays. It must be remembered that in most experimental work the criterion of death based upon the counting of colonies which grow in media inoculated by irradiated organisms is really a criterion of the failure of cell division to occur at the normal rate.

Gates [34] employed a quartz monochromator to separate the wave-lengths emitted by a quartz mercury arc, and measured the intensity at the exit slit by means of

[25] Rahn, O., [*J. Gen. Physiol.,* **13,** 179, 395; **14,** 315] has assumed that each cell contains one or several extremely sensitive molecules, the destruction or inactivation of any one of these preventing the multiplication of the cell. He believes that it may be necessary for more than one molecule to be destroyed in order that a yeast cell may be killed. In the case of the spores of the mold *Botrytis cinerea,* the number of reacting molecules is thought to be greater than one; and in the flagellate *Colpidium.* Rahn believes that two molecules must be destroyed before mobility ceases.

[26] Henri, V., *Compt. rend. soc. biol.,* **73,** 323.

[27] Harris, F. I., and Hoyt, H. S., *Pathology,* **2,** 245 (1919); *Chem. Abs.,* **13,** 2384 (1919).

[28] Henri, Mme., *Compt. rend.,* **158,** 1032 (1914).

[29] Galeotti, G., *Ann. Inst. Pasteur,* **30,** 49 (1916); *Chem. Abs.,* **10,** 2358 (1916).

[30] Bovie, W. T., and Hughes, D. M., *J. Med. Research,* **23,** 223 (1918).

[31] Henri, Mme., *Electrical Review,* **74,** 768 (1914).

[32] Eberson, F., *J. Immunol.,* **5,** 345 (1920); *Chem. Abs.,* **14,** 3273 (1920).

[33] Gates, F. L., *Science,* **58,** 479 (1928).

[34] Gates, F. L., *J. Gen. Physiol.,* **13,** 231 (1929).

thermopiles. A suspension of *Staphylococcus aureus* was flowed over an agar plate and exposed at the exit slit. After the exposure, this was covered with another layer of agar and incubated. The area counted coincided with the area of the thermopile junction. The energies applied were varied by altering the times of exposure. From a large number of experiments, smooth curves were obtained for the variation in the per cents of bacteria killed with variation in the logarithms of the available energies expressed in ergs per square millimeter.[35] The curves were so similar as to indicate that the reaction at any one wave-length is typical of them all. The form of the S-shaped curves is one frequently encountered in experimental biology. Four conclusions were drawn from this work.

1. No bacteria succumb in the initial period of exposure. The energy incident during this initial period is between 6 and 7 per cent of that required to kill all of the organisms.

2. After this period, between 20 and 30 per cent of the organisms were found to be destroyed by less energy than would be predicted from the rate of destruction of the remainder of the organisms. They seem to be less resistant than the rest.

3. A considerable proportion of the remaining bacteria (about 70 or 80 per cent of the total number) succumb along an energy gradient that bears an exponential relationship to the lethal effect, *i.e.,* a straight line. In other words, the middle portion of the curve may be reproduced by the equation describing the course of a monomolecular reaction.

4. In the final period there are remaining a number of organisms which are killed only by an excess of energy.

The second feature discussed above is attributed to the fact that young bacteria are less resistant than are older, resting organisms, a fact which had been demonstrated by Bang.[36] Gates was of the opinion that there was no evidence in his work that sublethal doses exerted any stimulating effect on the subsequent multiplication of bacteria, although this had been claimed by Browning and Russ.[37] This may have been due to the fact that when few bacteria survive in the middle of an exposed area, or when relatively few are left at the edges where the intensity of the radiation falls away, the colonies they produce are always much larger than those in the more crowded areas of the plate. The reason for the more active multiplication and consequent large colonies under these circumstances Gates believed to be merely that the nutrient substances per colony are not so limited, and also that waste products do not accumulate so rapidly.

One point of view regarding the nature of the lethal process disregards the features indicative of individual differences in the resistance of the organisms and considers the curve evidence for a fundamental monomolecular reaction underlying the process. Another point of view, to which Gates inclined, regards the course as determined by probability considerations and suggests that it should be compared with the mortality curves of insurance statistics. The similarity of the middle portion of the curve to that of monomolecular reactions is ascribed to a coincidence in the distribution of the resistance factors.

Gates showed [38] that wide variations in the intensities of incident ultraviolet energy (from 21.6 to 5.6 ergs per sq. mm.) were not accurately compensated for by making the appropriate changes in the times of irradiation. Thus the Bunsen-

[35] Hertel, E., [*Z. allgem. Physiol.,* **4,** 1 (1904); **5,** 95 (1905)] had made a beginning in this type of work, but he had reported only on the effects of six lines. Compare also Bang, S., *loc. cit.*

[36] Bang, S., *Mitteilungen aus Finsen's Lichtinstitut,* **2,** 1 (1901).

[37] Browning, C. H., and Russ, S., *Proc. Roy. Soc.,* **110,** 33 (1917).

[38] Gates, F. L., *J. Gen. Physiol.,* **13,** 249 (1929).

Roscoe reciprocity law does not hold strictly. The deviations were most marked with young organisms, metabolically and genetically active.

An exposure of thirty minutes at 3340 or 3660A failed to reduce the subsequent formation of colonies. Although the first experiments with 3130A indicated some bactericidal action, in later ones in which stray reflected light was more rigorously excluded, even very large incident energies had no appreciable effect.

No attempt was made to determine the short wave-length limits of lethal action. Weak lines at 2340, 2300 and 2250A required such long exposures that it was possible to establish only the middle portion of the curve of lethal action. Lyman [39] showed the bactericidal effects of radiations shorter than 1860A and Bovie [40] extended the lower limit to 1250A by the use of a hydrogen discharge tube and fluorite windows.

The lethal action has a temperature coefficient of 1.1, in agreement with the observations of Baynes-Jones and van der Lingen. Gates was unable to confirm the results of Thiele and Wolf,[41] and of Wiesner [42] who found an increase in temperature to extend the bactericidal zone toward the longer wave-lengths.

Variations in the pH of the medium between 4.5 and 7.5 were without influence on the lethal action, but at pH 9 and 10 there was a slight but definite increase in bacterial sensitivity. Plane-polarization of the incident ultraviolet light had no effect upon bactericidal action.[43]

Although the killing curves obtained by the use of different wave-lengths are similar in form, they lie at very different energy levels.[44] Thus energy required to kill half of the exposed organisms ranges from 3150 ergs per sq. mm. at 3020A to only 88 at 2660A. The latter wave-length has been reported to be optimum for killing organisms, longer or shorter ones requiring more incident energy. On plotting against the wave-lengths as abscissae the reciprocals of the energies required at various wave-lengths to kill half of the organisms, the curves showed a maximum at 2660A, a minimum near 2400A and another maximum beyond 2300A. A similar curve was obtained for *B. coli*.[45] Absorption curves of thin films of the organisms pressed between quartz plates were strikingly similar to the curves for the reciprocals of the energies required.

Comparatively few references are available on the absorption of the materials of the cell nucleus. Dhéré in 1906 stated that 4-methyluracil exhibits an absorption band between 2346 and 2801A. Since this was very similar to the absorption observed in the case of nucleic acid, he attributed the absorption spectrum of the latter to its pyrimidine and purine components. Holiday [46] more recently reported quantitative data on the absorption spectra of several purines.

Heyroth and Loofbourow [47] gave absorption curves for a number of purines and pyrimidines and showed that the absorption of thymonucleic acid may be represented as the summation of the molar extinction coefficients, at least at 2600A of

[39] Lyman, T., "Spectroscopy of the Extreme Ultraviolet," Longmans, Green and Company, pp. 1-3, 2nd ed., London, 1928.

[40] Bovie, W. T., *Bot. Gaz.*, **61**, 1 (1916).

[41] Thiele, H., and Wolf, K., *Arch. Hyg.*, **60**, 29; *Chem. Abs.*, **1**, 1029 (1907).

[42] Wiesner, R., *Arch. Hyg.*, **61**, 1 (1907).

[43] Bhatnagar, S. S., and Lal, R. B., [*Nature*, **117**, 302 (1926)] had previously suggested as a result of preliminary experiments on *B. typhosus* and *Vibrio cholerae* that bacterial life is favorably affected by polarized light as compared with ordinary light of equal intensity.

[44] Gates, F. L., *J. Gen. Physiol.*, **14**, 31 (1930). *Cf.*, however, Herčik, F., *J. Gen. Physiol.*, **20**, 589 (1937).

[45] For *E. coli*, V. Henri finds the maximum bactericidal action at 2750A. *Festschr. Zangger*, **2**, 792 (1935); *Ber. ges. Physiol. exptl. Pharmakol.*, **86**, 363; *Chem. Abs.*, **31**, 6683 (1937).

[46] Holiday, E. R., *Biochem. J.*, **24**, 619 (1930).

[47] Heyroth, F. F., and Loofbourow, J. R., *J. Am. Chem. Soc.*, **53**, 3441 (1931); **56**, 1728 (1934).

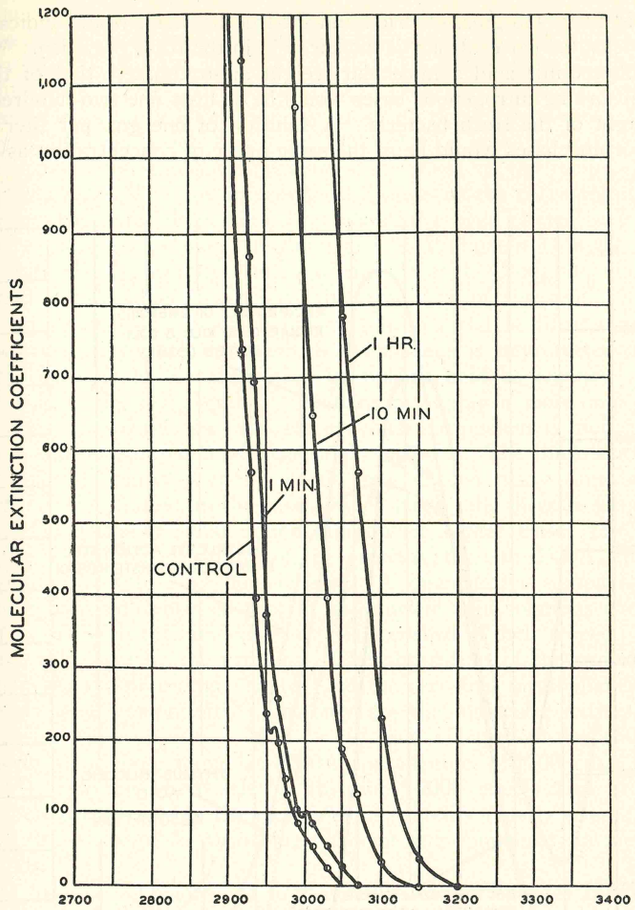


FIGURE 133. Absorption of Uracil at one gram per liter, Showing Effect of Irradiation with Full Ultraviolet (Heyroth and Loofbourow, *Journal American Chemical Society*).

adenine, guanine, cytosine and thymine. They advanced arguments for viewing their absorption data as supporting the hypothesis of Gates that it is energy absorbed by these cellular components which is concerned in the lethal mechanism.[48] The absorption of the typical pyrimidine, uracil, in a concentration roughly comparable to that estimated as present in the cell nucleus, rises very abruptly and rapidly at about 2950A. This is the wave-length found by many workers to represent the approximate lethal threshold for the rapid action of ultraviolet rays on bacteria. (See Figure 133.) The concentration of one gm. per liter was chosen for these measurements because of the following considerations. Assuming for tubercle bacilli a water content of 70 per cent and in the dried material a fat content of 40 per cent, the work of Johnson and Brown, who obtained 7.7 gms. of a

[48] Heyroth, F. F., and Loofbourow, J. R., *Bull. Basic Sci. Research*, **5**, 13 (1933).

nucleic acid from 436 gms. of dried and fat-free bacteria, would indicate the presence of at least 0.3 per cent of this nucleic acid in the fresh organisms.[49] Assuming for this tuberculinic acid a molecular weight approximately that of thymonucleic acid, the absorbing nitrogenous bases would be at least one two-hundredth per cent of the weight of the fresh bacteria. A solution of one gm. per liter of any one of the absorbing bases would be of the same order of concentration as in the fresh bacteria.

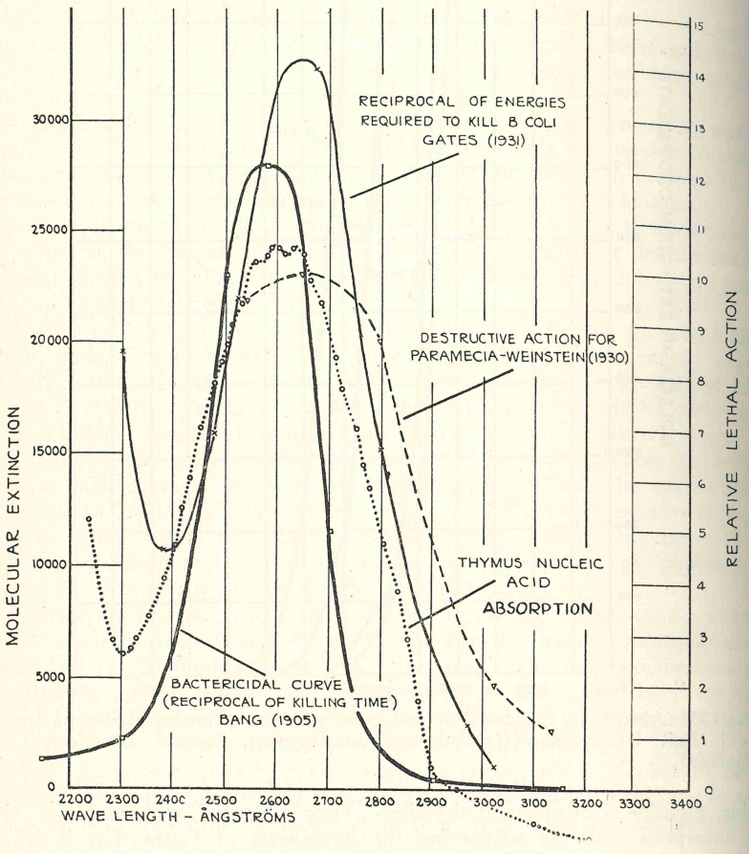


FIGURE 134. Comparison of Lethal Action of Ultraviolet and Absorption of Nuclear Materials. (Heyroth and Loofbourow, *Bull. Basic Sci. Research.*)

It is apparent that the absorption curve of these pyrimidine and purine bases in concentrations comparable to those found in the cell corresponds closely to the lethal threshold for the killing of microörganisms. As indicated by the figure, this long-wave absorption curve for high concentrations of the nuclear materials moves toward still longer wave-lengths during the irradiation of these substances with unfiltered ultraviolet light. This produces a filtering effect which tends to

[49] Johnson, T. B., and Brown, E. B., *J. Biol. Chem.*, **54**, 721 (1922).

screen the unchanged substances from the destructive action of the radiations. It is a matter of extreme interest that this occurs particularly with respect to the shortest wave-lengths that may be found in the solar spectrum as available on the surface of the earth.

The point of maximum absorption by most of these pyrimidine and purine bases and by nucleic acid itself lies near 2600A.[50] To make clear the similarity between the forms of these absorption curves and those of the reciprocals of the energies required for killing, and interpreted by Gates as the curve for the absorption by the sensitive materials in the cells, curves have been plotted in Figure 134. These compare the data of Gates, of Bang and of Weinstein (for the killing of Paramecia) with the[51] absorption curve of nucleic acid. Both the nucleic acids from yeast and from thymus glands have the same type of absorption curve.

Only in those organisms in which the nuclear material is diffused throughout the cell (bacteria and yeasts) or in which the nucleus is unprotected by a thick layer of cytoplasm should the absorption by nucleic acid be expected to play a predominant role in the lethal action. Proteins may play a more important role in the effects on cells such as the protozoa in which the nucleus is more adequately protected by a thicker surrounding layer of protoplasm. The thickness of such a cytoplasmic layer in many of the protozoa may exceed many times the entire diameter of bacteria. Indeed, in the case of such large cells there is some evidence to show that the optimum lethal action takes place rather closer to 2800A, the position of the absorption maximum of the proteins, than to 2600A, the position of the maximum absorption by nucleic acid. A quantitative comparison of the absorption of equally concentrated protein and nucleic acid solutions shows that a far greater proportion of the incident energy is absorbed at their respective maxima by the nucleic acid than by the proteins. The absorption of the proteins in this region is due (see the preceding chapter), to the tyrosine, tryptophane and other aromatic amino- acid components. Not only are the molecular extinction coefficients of tyrosine (approximately 2000 $cm.^{-1}$), and of tryptophane (5000 $cm.^{-1}$) at 2800A lower than those found at 2600A for adenine (10,300 $cm.^{-1}$), guanine (12,000 $cm.^{-1}$), cytosine (6100 $cm.^{-1}$), thymine (9000 $cm.^{-1}$) and uracil (9100 $cm.^{-1}$), but their proportions in the molecules of proteins (rarely over 2 per cent) are much less than those of the absorbing nitrogen ring compounds in the molecules of nucleic acids.

Relatively little is yet known as to the nature of the changes induced in the pyrimidines by the action of ultraviolet rays. The absorption spectrum changes during irradiation in the manner indicated in Fig. 135.[52] The molecular extinction curve of uracil is given in the upper heavy curve (concentration of 10 mg. per liter). During the first few minutes of irradiation with full ultraviolet light from a mercury arc there is a definite rise in absorption in the region from 2200 to 2300A and also in the region of wave-lengths longer than 2900A. During the later periods of irradiation, the absorption of the head of the band decreases. In the case of uracil this change occurs after fifteen minutes of exposure at 2 cm. from a Victor water-cooled arc. For a time the rise in absorption at both legs of the curve continues although the absorption at the center of the band is diminishing. After about fifteen minutes, however, the absorption between 2200 and 2300A also begins to decrease, although that of the rays of wave-length longer than 2900A continues to increase for three hours and then decreases. If the radiation

[50] Heyroth, F. F., and Loofbourow, J. R., *J. Am. Chem. Soc.*, **53**, 3441 (1931).
[51] Weinstein, I., *J. Opt. Soc. Am.*, **20**, 433 (1930).
[52] Heyroth, F. F., and Loofbourow, J. R., *J. Am. Chem. Soc.*, **53**, 3441 (1931).

is sufficiently prolonged, practically all selective absorption is lost, the absorbed energy causing photochemical changes which destroy the pyrimidines. In the case of nucleic acid, an irradiation of an hour caused but negligible change between 2500 to 2900A, but in the region near 2300A the extinction coefficients increased nearly 45 per cent. The position of the minimum shifted slightly toward longer wave-lengths during this period. On more prolonged irradiation the absorption at the head of the band decreased.

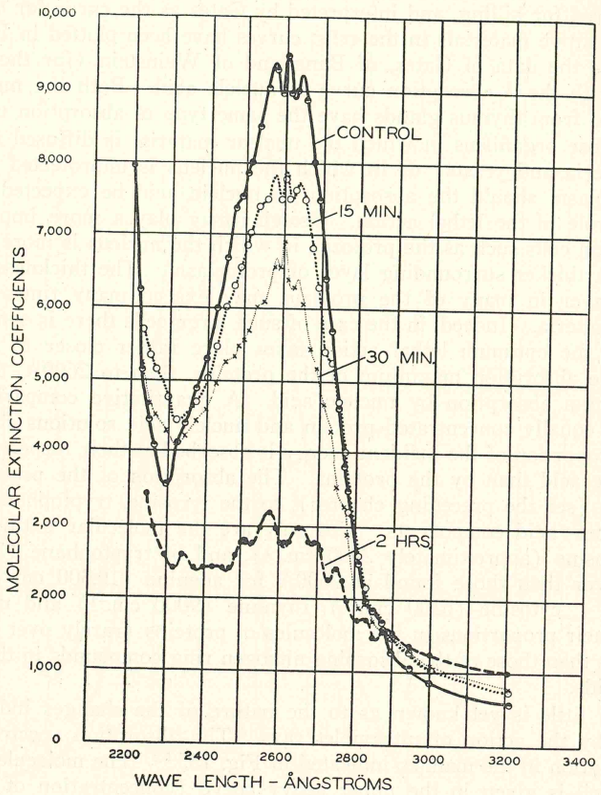


FIGURE 135. Effect of Ultraviolet Irradiation upon the Absorption Spectrum of Uracil. (Heyroth and Loofbourow, *Journal American Chemical Society.*)

The mechanism underlying these changes is as yet unknown. There may be either a rupture of the ring with the production of diactinic products of the nature of urea and open-chain three-carbon compounds, or there may be a gradual saturation of the ring. Bass has shown that thymine, after twelve hours of ultraviolet irradiation in the presence of oxygen and ferrous salts, yields urea and pyruvic acid.[53] Lieben and Getreuer,[54] state that no ammonia is liberated during the irradiation of uric acid, xanthine, uracil, alloxan, hydantoin and α-hydroxynicotinic acid. There is, however, evidence of an increase in free amino- groups

[53] Bass, L. W., *J. Am. Chem. Soc.*, 46, 190 (1924).
[54] Lieben, F., and Getreuer. V., *Biochem. Z.*, 259, 1 (1933).

indicative of a rupture of the ring. Sodium nucleate is relatively resistant to rupture. Histidine, proline, guanine, pyridine and nicotinic acid evolve ammonia. In these cases the destructive effect apparently is hastened by oxygenation, but the latter is not essential to the change.

It was suggested by Heyroth and Loofbourow that the early change might involve the formation of a compound of the type of α-isouracil described by Tafel and Houseman.[55] Since the formula proposed by those workers involved the presence of a hydroxyl group in position five, and since Johnson and Johns[56] had concluded that the ability of pyrimidine compounds to reduce phosphotungstic acid in alkaline solution depends on the presence of amino- or hydroxyl groups in this position, Heyroth[57] investigated the effect of irradiation upon the ability of uracil to reduce this reagent. It was found that irradiation of a uracil solution induces a photochemical change resulting in the formation of a substance or substances capable of reducing an arsenophosphotungstic acid solution. The rate of change was greatest early in the irradiation. The observation of the occurrence of this reaction may be of aid in the interpretation of certain findings in the physiology of irradiation. Clinical observations of an 80-per cent increase in the blood uric acid and purines have been reported by Wiener[58] to occur in patients undergoing phototherapy. Koch and Reed[59] reported a 38-per cent increase in the blood uric acid of a dog during irradiation with a carbon arc for an hour and a half. The blood was irradiated while flowing through quartz tubes introduced into the circulation. These authors did not attribute the increased values to the formation of uric acid but instead to the presence of some substance giving a similar reduction of the uric acid reagent (phosphotungstic acid) used for the determination of the so-called blood uric acid. Dillman[60] could not obtain the increase when the blood was irradiated *in vitro*. He also noted that irradiation of uric acid destroys its ability to reduce phosphotungstic acid. The observations on uracil suggest the purine or pyrimidine nucleosides of the blood as a possible source from which such a reducing substance might be formed during irradiation. Pincussen and Flores[61] by experiments *in vitro* attempted to learn something of the fate of nucleins exposed to radiations. Specimens of nucleic acid were exposed to the rays of a Nitra lamp, the heat rays being removed by a water filter. Eosin and dichloroanthracene were tested as sensitizing agents, and the changes in the specific rotation of the solution of nucleic acid were followed. A splitting of the acid was pronounced without sensitizer or in the presence of eosin, but was not detected in the presence of the anthracene compound. The nucleic acid-splitting enzymes did not appear to be increased when animals were irradiated.

Ultraviolet photomicrographs of the chromosomes of *Drosophila* in various fluid reagents have been given by Hellström, Brandt and von Euler.[62]

Peptization of cell colloids was obtained when a sharp pencil of ultraviolet light was passed into the macronuclei of *Paramecium caudatum, Spirostomum ambiguum,* and *Amphileptus claparedei.*[63] Microscopic ultraviolet absorption methods have been employed to follow the distribution of nucleic acid in tissues during the proc-

[55] Tafel, J., and Houseman, P. A., *Ber.*, 40, 3743 (1907).
[56] Johnson, T. B., and Johns, C. O., *J. Am. Chem. Soc.*, 36, 970 (1914).
[57] Heyroth, F. F., *Bull. Basic Sci. Research*, 4, 128 (1932).
[58] Wiener, H., *Klin. Wochschr.*, 3, 936 (1924).
[59] Koch, F. C., and Reed, C. I., *Am. J. Physiol.*, 75, 351 (1925).
[60] Dillman, L. M., *J. Lab. Clin. Med.*, 17, 44 (1931).
[61] Pincussen, L., and Flores, A., *Biochem. Z.*, 126, 86 (1921). See also Chapter 33.
[62] Hellström, H., Brandt, K., and von Euler, H., *Svensk Kem. Tids.*, 47, 249 (1935); *Mikrochemie, Festschr. Hans Molisch,* 2093 (1936).

esses of mitosis and glandular secretion.[64] In the large chromosomes of *Stenobothrus* spermatocytes, the absorption curves correspond to those of a 15-per cent solution of thymonucleic acid. Chromosomes are built up of alternating nucleic acid segments and protein segments.[65]

Interesting observations of another type relating to the effect of ultraviolet rays in killing *Escherishia coli* have been reported by Lisse and Tittsler.[66] By the use of either Northrop-Kunitz or Falk capillary electrophoresis cells, they found that irradiation, if of sufficient duration, produces a decrease in the negative charge of the organism. With the former type of cell they found some indication of an initial stimulative action of the ultraviolet radiations which made itself felt in an increase of the negative charge. This could not, however, be observed with the Falk capillary cell. Short irradiations which merely stimulate or injure the cells permit a return of the electrokinetic velocity toward its normal value, but prolonged lethal irradiation produces a lasting effect. The sequence of decreasing electrophoretic velocities is the same as that of increasing susceptibility to agglutination except in the case of very long or very short irradiations. The interposition of a Corex A filter causes a practical disappearance of this sequence of agglutinability. Irradiation by a carbon arc also produced lysis which was the greater the longer the irradiation. Irradiation produced an increase in the pH of an aqueous suspension of cells, the original pH of which was approximately 6.1. With 500-watt Mazda bulbs as the light source there was eventually a reduction of the charge and evidence of lysis indicated by a clearing of the suspension, but much longer times of irradiation were required than when ultraviolet light was used. Norton[67] also suggested that the changes suffered by bacteria on exposure to ultraviolet rays may be accompanied or perhaps preceded by changes in the electrical charges borne by the bacteria.[68]

Gärtner[69] finds the agglutinability of bacterial suspensions to be increased and the zone of acid agglutination widened by irradiation, although the acid zone is narrowed by prolonged exposures. Basic dyes agglutinate irradiated bacteria in lower concentrations. The pH is increased and the acid-binding power decreased. Agglutinability with antiserum is decreased.

Pincussen and Gutfeld[70] studied the influence of salt solutions on the killing of various organisms by light. With *Staphylococcus aureus,* the killing effect in calcium chloride solutions was about three times that obtained in distilled water, but other salts, including the chlorides of sodium, potassium and magnesium, were without this influence. Calcium chloride had a protective action on the diphtheria bacillus, the action of light being about four times greater in distilled water. Ehrismann[71] studied the effect of various cations in inhibiting the lysis or clearing of suspensions of bacteria. The process is recognized by a decrease in the volume

[63] Tchakhotine, S., *Compt. rend.,* **202,** 778 (1936).

[64] Casperson, T., *Skand. Arch. Physiol. Suppl.,* **8,** 151 pp. (1936): *Bull. histol. appl. physiol. path. tech. microscop.,* **14,** 33 (1937): *Protoplasma,* **27,** 463 (1937); Casperson, T., Hammarsten, E., and Hammarsten, H., *Trans. Faraday Soc.,* **31,** 367 (1935).

[65] Casperson, T., *Naturwiss.,* **23,** 527 (1935).

[66] Lisse, M. W., and Tittsler, R. P., *Proc. Soc. Exp. Biol. Med.,* **28,** 811 (1931).

[67] Norton, J. F., in Jordan, E. O., and Falk, J. S., "Newer Knowledge of Bacteriology and Epidemiology," Univ. of Chicago Press, 374 (1928).

[68] For other references to this work, see Lisse, M. W., *Penn. Agr. Sta. Tech. Bull.,* **230,** 6 (1928); **243,** 6 (1929); **258,** 8 (1930); Tittsler, R. P., and Dozois, K. P., *Ibid.,* **258,** 28 (1930); Lisse, M. W., Tittsler, R. P., and Sharpless, G. R., *Ibid.,* **276,** 4 (1932). The last includes an exhaustive bibliography on the lethal action of ultraviolet rays.

[69] Gärtner, I., *Z. Immunitäts,* **80,** 493 (1933); *Chem. Abs.,* **28,** 5491 (1934); Gärtner, I., and Szathmary, J., *Z. Immunitäts,* **78,** 249 (1933).

[70] Pincussen, L., and Gutfeld, F. V., *Centr. Bakt. Parasitenk., 1 Abt.,* 109 (1928).

[71] Ehrismann, O., *Z. Hyg. Infektionskrankh.,* **111,** 618 (1930); *Chem. Abs.,* **25,** 721 (1931).

of the suspended particles or by the appearance of nitrogenous compounds in the surrounding fluid. An accelerated decomposition of the bacterial proteins into amino- acids could not, however, be demonstrated. The following cations inhibit the action in the order indicated: $La^{++} > Ca^{++} > Ba^{++} > Sr^{++} > Mg^{++} > Na^{+}$ or Li^{+} or K^{+}. Also an increase in temperature, displacement of the pH to the acid side, the addition of formaldehyde or of mercuric chloride inhibit decomposition. The various bacteria studied could be arranged in a series according to their sensitiveness.

Number of Quanta Per Bacterium Required for Killing. The question has been raised as to the number of quanta which must hit a single organism, which of course is itself a system containing many molecules, in order to kill it. The reasoning involved has been discussed by Wyckoff for killing bacteria by high-velocity electrons,[72] where it appeared that the absorption of a single high-voltage electron by a colon bacillus was sufficient to cause death.

In the case of the killing by x-rays,[73] Wyckoff found that the absorption of a single x-ray quantum of energy sufficed to kill an organism, although only about one in twenty of the absorbed quanta was effective. From this he concluded that within the organism there is some sensitive region the destruction of which leads to death, and that this sensitive "cell" must have a volume less than 6 per cent of the bacterium itself.

The case is somewhat different in the lethal action of ultraviolet rays. Wyckoff[74] interpreted the results of Gates on *Staphylococcus aureus* as indicating curves of a "multiple-hit-to-kill" type. Since he believed that the tendency of this organism to cling together in chains made it impossible to spread them properly, he repeated the experiments with the more motile *B. coli.* Survival-ratio curves at various wave-lengths when plotted on semilogarithmic paper gave straight lines, indicating an exponential killing rate. This might be due either to a single quantum-hit killing the organism or to a suitable distribution of the sensitivities of the bacteria. The slope of these curves at all wave-lengths less than 3000A indicated an average number of effective absorptions per bacterium per second of somewhat less than 0.03. From the intensity of the energy and the volume of the bacterium, it could be calculated that for the 2699A line, the radiant energy absorbed per bacterium per second was 0.99×10^{-6} erg. Since each quantum at this wave-length represents 7.25×10^{-12} erg, the total number of quanta absorbed per bacterium per second was calculated to be 136,000. But of these, less than one (0.03) was effective in causing death. Thus only 0.03/136,000 or one in 4.19×10^{6} of the absorbed quanta was effective. Wyckoff then proceeded to multiply the volume of one bacterium (3.93×10^{-13} cc.) by a fraction 0.03/136,000 and thus obtained what he considered to be a sensitive volume, which was 9.38×10^{-20} cc. As it could be calculated that this is approximately the volume which might be occupied by an average-sized protein molecule, it was possible to make the suggestion, although with reservations, that the lethal action depends upon an effect upon one protein molecule in the organism. That the explanation was unlikely was indicated by the fact that the millions of non-lethal quanta absorbed per bacterium did not cause any alteration in the growth rate. However this may be, the data indicate for the organism a very low quantum yield. In liquid or solid systems low quantum yields do not necessarily imply the existence of some unusually sensitive substrate molecule or unit cell. Other explanations of the low quantum yield will undoubtedly

[72] Wyckoff, R. W. G., *J. Exp. Med.,* **51,** 921 (1930).

[73] Wyckoff, R. W. G., *J. Exp. Med.,* **52,** 435, 769 (1930).

[74] Wyckoff, R. W. G., *J. Gen. Physiol.,* **15,** 351 (1932).

be advanced when the photochemical reactions leading to the death of the organism are better understood.

In general, Wyckoff found the energies required to kill half of the organisms at various wave-lengths to be of the same order as those reported by Gates. Like Gates, he found that the greatest effectiveness lies at about 2652A. There are, however, some discrepancies between the energies found by Gates and by Wyckoff, for which no explanation is yet apparent. It is also interesting to note that Wyckoff found at 3132A that the curve for survival-ratios against time could not be indicated on semilogarithmic paper by a straight line with the same accuracy as the curves obtained at other wave-lengths. It seems possible that the mechanism of killing at wave-lengths longer than 2900A is different from that at the shorter wave-lengths.

Evidence for a variation in the resistance of individual cells has occasionally been noted, particularly in the work of Gates previously discussed. Beauverie[75] finds that the resistance of yeast cells increases in proportion to their glycogen content.

Although all microscopic living forms can be killed by ultraviolet light, they exhibit varying degrees of resistance either inherent and specific to the organism, or extrinsic and due to the conditions of the irradiation. Among themselves bacteria show considerable, and to some extent characteristic, variations of resistance from species to species. But an attempt to employ these variations for the differentiation of bacteria was unsuccessful.[76] Nogemi[77] finds that *Es. coli,* streptococci and the cholera vibrio are killed readily and that the tubercle and anthrax bacilli are more resistant. In general spores are somewhat more resistant than vegetative forms.[78]

Sunlight has a deleterious action on cultures of *Brucella abortus,* sterilizing them in three hours. Ultraviolet light has a similar effect.[79]

According to Mayer and Dworski,[80] a suspension of tubercle bacilli containing 2,750,000 organisms per cc. was killed within four minutes by the absorption of 1.42×10^{9} ergs per sq. cm. from unfiltered radiations of the quartz mercury arc. Exposure to an intensity of 5.93×10^{6} ergs per sq. cm. per second for 25 minutes did not alter the acid-fast staining qualities of these organisms. When fixed by heat and irradiated for 5 to 25 minutes, the bacilli showed changes indicative of disintegration, since irregularities were observed on staining by the Ziehl-Neelsen method.

Akiyama[81] claims that *Es. coli, Sal. typhimurium* and staphylococci in salt solution are more resistant to ultraviolet light when sensitized with their own specific serums than when treated with heterologous immune serums or with normal serum. The bacteria treated with the globulin fraction of the specific immune serums are more resistant than those treated with the albumin fractions of the same serums.

Bacteria killed by ultraviolet light lose a considerable part of their toxicity toward laboratory test animals, but completely retain their antigenic and immunizing characteristics.[82]

[75] Beauverie, J., *Compt. rend.,* **199,** 81 (1934).
[76] Browning, C. H., and Russ, S., "Applied Physiology," p. 150, Oxford University Press, 1918.
[77] Nogemi, Y., *Kitasato Arch. Exp. Med.,* **10,** 135 (1933).
[78] Lagerberg, O., *Z. Immunitäts.,* **28,** 186 (1919); *Chem. Abs.,* **13,** 2385 (1919).
[79] Morales-Otero, P., *Puerto Rico J. Pub. Health & Trop. Med.,* **6,** 1 (1930).
[80] Mayer, E., and Dworski, M., *Tubercle,* **13,** 500 (1932).
[81] Akiyama, M., *Sei-ikai Med. J.,* **54,** No. 5, 840 (1935); *Chem. Abs.,* **30,** 3018 (1936).
[82] Trotskii, V. L., Sviridova, T. A., and Super, L. P., *J. Microbiol., Epidemiol., Immunobiol.,* **15,** 519 (1935); *Chem. Abs.,* **30,** 4531 (1936).

Recently, Hollaender and Claus[83] have given data on the energy required for the inactivation of *Es. coli* as a function of the wave-lengths employed. At 2250A, the ergs required per bacterium were 41.3×10^{-6}; at 2650A, 13.1×10^{-6}; and at 2950A, 81.6×10^{-6}. These values were regarded as somewhat more accurate than those cited in preceding paragraphs since they were calculated by a method which corrected for the protective action of nonviable organisms.

Lehner[84] states that although *Rhodovibrio* is killed quickly by ultraviolet rays, *Thiocystis* is not killed by an exposure of an hour, and that short exposures accelerate growth.

Action of Ultraviolet Rays on Yeast

Lacasagne[85] exposed *Saccharomyces ellipsoideus* to radiations of wave-lengths between 2800 and 3800A and found the cells to fall into three classes according to their susceptibility to the rays. Some died immediately, some after a certain period and others exhibited only a retarded rate of cell division but ultimately recovered their power of reproduction. Wyckoff and Luyet[86] made similar observations and noted the production of some giant cells. Their results tended to indicate "multiple-quantum-hit" relations.

In the work of Oster[87] carefully prepared suspensions of *Saccharomyces cerevisae* containing practically no clumps of cells were employed. Following irradiation, observation with a microscope revealed certain abnormalities in cell growth and reproduction. There was apparent a period of survival during which normal colonies could not be formed, after irradiation by each of the wave-lengths (2225 to 3132A) studied. There could be distinguished single cells of normal size and not visibly altered, single cells of giant size, two-cell groups usually from three to eight times the size of normal two-cell groups and more spherical in shape and often showing a long filament-like process constricted at intervals along the length, three to eight-cell groups of giants, which at this stage either cease budding or go on to furnish buds of normal size, and finally larger groups which, although retarded in their ability to form normal-sized colonies show little evidence of giantism. At all wave-lengths, a definite, measurable retardation in reproduction as based upon the criterion of culture formation could be demonstrated. The size of the colonies increased at a rate roughly proportional to the increase in incident energy. The relation between the percentage of inhibition and the incident energy appeared to be logarithmic over the inhibitory range. When the period of exposure was increased beyond this point, various degrees of injury occurred and finally all budding and growth could be stopped. As a criterion of lethal action, Oster adopted the inability of the yeast cell to form two or more daughter cells rather than merely the inhibition of macroscopic colonies. The survival-ratio is then the ratio of the number of cells which bud at least twice to the original number of exposed cells. For each of several wave-lengths shorter than 2900A curves were plotted of the survival-ratio against the energy in ergs per sq. mm. In the case of longer wave-lengths very much more incident energy was required for lethal effects.

The curves revealed that for all wave-lengths studied the energy which had to be applied before any of the cells were killed was approximately 8 per cent of that required

[83] Hollaender, A., and Claus, W. D., *J. Gen. Physiol.,* **19,** 753 (1936).
[84] Lehner, A., *Zentr. Bakt., Parasitenk., (Abt. II),* **97,** 65 (1937); *Chem. Abs.,* **32,** 1743 (1938).
[85] Lacasagne, A., *Compt. rend.,* **190,** 524 (1930).
[86] Wyckoff, W. R. G., and Luyet, B. J., *Radiology,* **17,** 1171 (1931).
[87] Oster, R. H., *J. Gen. Physiol.,* **18,** 71 (1934-5).

to kill all the cells. Between 20 and 30 per cent of the cells do not survive after an exposure relatively short in comparison with that required to suppress budding in all of the cells. The remaining 70 or 80 per cent require from 70 to 80 per cent of the energy required to kill all the cells. The last 2 or 3 per cent of the cells are affected at a slightly lower rate. Cells irradiated with small amounts of energy show a much lower rate of budding with a longer initial lag period than that of the typical growth curve of normal cells. The age of the cells has a marked influence upon their resistance, from 20 to 50 per cent more energy being required to produce a given effect on a fifteen-day culture than on 24-hour cultures. In the former, a greater proportion of the cells is in the resting stage.[88]

The temperature coefficient is low, about 1.06 to 1.1, in agreement with that obtained by Gates on bacteria. The irradiation effects are exerted directly upon the organisms since irradiation of the malt-agar medium for periods from five minutes to two hours had no effect upon the growth of organisms subsequently planted in it. For intensity variations up to 30 per cent, the rate of absorption of photons by the cells did not markedly affect the lethal action.

Attempts to determine the absorption spectrum of yeast failed to give satisfactory results. However, an application of the method of Gates of plotting the reciprocals of the energies required to cause death in 50 per cent of the cells against the wave-lengths employed, gave results similar to those reported by Gates for bacteria. The necessary energies ranged from 457 ergs per sq. mm. at 2652A to 23,500 ergs at 3022A, or roughly five times the energy range for *Staphylococcus aureus.*

From the individual survival-ratio curves plotted against the incident energies applied, Oster calculated (by a method devised by Curie,[89] which differs somewhat from that employed by Wyckoff), the number of quantum-hits necessary to kill at various wave-lengths. The results indicated a "multiple-quantum hit-to-kill" relation, the minimum number of quantum hits varying from about four to about six. The shape of the curves was believed to suggest that other factors than single quantum hits on several molecules are involved, as suggested by Rahn, or multiple-quantum hits on a sensitive volume element, as suggested by Wyckoff and Luyet.

Stimulation of Yeast. There have been many attempts to show the stimulation of yeast growth by irradiation by ultraviolet light. Some authors believed that wave-lengths somewhat longer than the lethal ones have such an action. Loofbourow and Cameron, who reviewed the literature,[90] were themselves unable to detect such an action, and this is the generally accepted conclusion.

There have, however, been suggestions that sublethal doses of radiation in the lethal wave-length range may produce injuries of the cells by virtue of which products capable of stimulating the growth of other cells are formed. Hollaender and Duggar[91] observed that cells from the 10 per cent which survived a certain irradiation in isotonic salt suspension by the 2650A rays increased in number when transferred to salt solutions (single or balanced) in which normal control cells died. Fardon, Norris, Loofbourow and Ruddy[92] claimed that substances which stimulate the respiration of other cells are produced in cells injured by ultraviolet light. Subsequently, these observers[93] devised a method for demonstrating the formation of growth-stimulating substances in the injured cells. The active substances were allowed to diffuse from the injured cells through an agar gel upon

[88] For comparison with the effects of x-rays at various stages of the reproductive period, see Lacasagne, A., and Holweck, F., *Compt. rend. soc. biol.*, **104,** 1221 (1930); *Compt. rend.*, **190,** 524, 527 (1930); *Compt. rend. soc. biol.*, **103,** 60 (1930); Strangeways, T. S. P., and Hopwood, F. L., *Proc. Roy. Soc.*, **100B,** 283 (1926); Holweck, F., *Congress Intern. Elec., Paris,* **10,** 1 (1932).

[89] Curie, M., *Compt. rend.*, **188,** 202 (1929).

[90] Loofbourow, J. R., and Cameron, J., *Bull. Basic Sci. Research,* **5,** 33 (1933).

[91] Hollaender, A., and Duggar, B. M., *J. Bact.*, **33,** 16 (1937).

[92] Fardon, J., Norris, R. J., Loofbourow, J. R., and Ruddy, M., *Nature,* **139,** 589 (1937); Fardon, J. C., Carroll, M. J., and Veronita, M., *Studies Inst. Divi Thomae,* **1,** 17, 41 (1937).

[93] Sperti, G., Loofbourow, J. R., and Dwyer, C. M., *Studies Inst. Divi Thomae,* **1,** 162 (1937).

the surface of which a fresh colony was placed. Colonies grew more rapidly on agar above injured cells than on agar above normal cells.

In earlier experiments, Pulkki[94] had been unable to produce a stimulant for *B. mycoides* by irradiation of yeast cells. Abderhalden[95] was unable to alter significantly the course of alcoholic fermentation due to yeast cells by the addition of alcoholic extracts of irradiated yeast, irradiated yeast macerated juice, or ergosterol. Woodrow, Bailey and Fulmer[96] believed irradiation of yeast culture media produces a non-volatile toxic material derived from the sugar present, but Oster was unable to detect any toxic substance liberated by the organism during its irradiation.

Suranyi and Vermes[97] claimed to have observed an increase of about 50 per cent in the oxygen consumption of yeast at pH 7.2 during irradiation. Oster, however, could detect no observable effects on oxygen consumption until more than 80 per cent of the organisms had been so affected that normal colonies did not result from their subsequent growth.

Teindl-Czech[98] found visible light to have no influence on the division rhythm of yeast cells. The same was true for very small exposures from an unfiltered Uviol lamp. Immediately after medium doses the number of cell divisions decreased: this was followed by a temporary rise and a new decrease. During irradiation the yeast appeared slightly vitreous and turbid. With strong doses, abnormal cell forms appeared. Irradiation by the region between 2300 and 4000A in the absence of oxygen may be used to secure yeast cells of uniform potency.[99]

Fermentation. Zeller[100] found sunlight to inhibit the output of carbon dioxide from yeast after a temporary slight stimulation. Guerrini[101] inoculated yeast into 5-per cent glucose solutions and incubated the cultures in darkness, in daylight and in light filtered through red, green, yellow and blue screens. He claimed to find the liberation of carbon dioxide to be greater in cultures exposed to light than in those in darkness. In general, the greatest quantities of carbon dioxide were produced in red light, the next greatest in yellow, then in green and the least in blue light. The last gave practically no carbon dioxide. Murakami[102] found that in the fermentation of koji extract the production of alcohol was maximal under a red light of wave-length longer than 6200A, increasing in general with the wave-length. The maximum yield of aldehyde was obtained under wave-lengths between 3960 and 5400A. Acetal was produced abundantly under a white light. The production of volatile acid was greatest in darkness and that of non-volatile acid greatest in violet to yellow light. The production of esters was generally higher under light of longer wave-lengths. There have been a number of claims that ultraviolet light increases the fermentative power of yeast.

Lindner[103] found that under normal conditions 30 gms. of dextrose gave 119 cc. of carbon dioxide in 24 hours and under ultraviolet irradiation 2743 cc. In the same

[94] Pulkki, L. H., *Ann. Acad. Sci. Fennicae,* **A41,** No. 1 (1935); *Chem. Abs.*, **30,** 4898 (1936).

[95] Abderhalden, E., *Fermentforsch.*, **9,** 195 (1927); *Brit. Chem. Abs.*, **A,** 1113 (1927).

[96] Woodrow, J. W., Bailey, A. C., and Fulmer, E. I., *Plant Physiol.*, **2,** 71 (1927).

[97] Suranyi, G., and Vermes, M., *Magyar Orvosi Arch.*, **30,** 585 (1929); *Chem. Abs.*, **25,** 2162 (1931).

[98] Teindl-Czech, L., *Protoplasma,* **27,** 313 (1937). Note also Palmieri, G. G., and Giordano, G., *Boll. soc. ital. biol. sper.*, **7,** 1318 (1932); *Chem. Abs.*, **27,** 1371 (1933).

[99] Light, R. F., Frey, C. N., and Patitz, G. J., U. S. P. 2,099,025, Nov. 16, 1937; *Chem. Abs.*, **32,** 300 (1938).

[100] Zeller, H., *Biochem. Z.*, **171,** 45 (1926).

[101] Guerrini, G., *Boll. soc. ital. biol. sper.*, **5,** 635, 1098 (1930); *Chem. Abs.*, **25,** 534 (1931).

[102] Murakami, R., *J. Agr. Chem. Soc. Japan,* **8,** 1237 (1932); **9,** 672 (1933); *Chem. Abs.*, **27,** 1983, 5470 (1933); *Bull. Utsunomiya Agr. Coll.*, **3,** 29 (1933); *Chem. Abs.*, **28,** 3519 (1934).

[103] Lindner, P., *Woch. Brau.*, **39,** 166 (1922); *Chem. Abs.*, **17,** 1686 (1923).

period[104] De Fazi[105] claimed to have observed a stimulation of growth and fermentation of yeast. His investigations involved in some cases irradiation of the water used in dissolving the sugar to be fermented rather than of the yeast or fermenting mixture. Even under the former conditions, some stimulation was stated to occur. Also, such claims have been made by Sanzo and Pirrone.[106]

Owen and Mobley[107] have reported that exposure of yeast to ultraviolet light increases its growth and its fermenting power. An exposure of one minute to radiations of wavelengths 2300 to 3100A gave the greatest stimulation, but an exposure of three minutes had the opposite effect. Since a similar stimulation could be brought about, they believed, by the irradiation of sterilized molasses wort, they did not attribute the stimulation to the death of harmful contaminating microörganisms. Beckwith and Donovick[108] exposed a 36-hour culture of purified brewers' yeast in a layer 1.15 cm. thick to ultraviolet radiations for 1.4 seconds per cc. Of the irradiated culture, 125 cc. were added to 1600 cc. of sterilized beer wort and incubated at 28°C. for 32 days. Alcohol formation was at first depressed, but from the 9th to 32nd days exceeded that in the control. Irradiation of the wort alone was without effect. Marmeli and Baratto[109] find that fermentation may be accelerated by addition of small quantities of such substances as ascorbic acid, β-carotene, acamnine, adenine, phytin or inosine. The effects were claimed to be enhanced by previous irradiation of these substances.

Tanner[110] found ultraviolet light to have only a depressing action on fermentation, whether the yeast, the fermenting culture or the glucose broth was the subject of the irradiation. According to Reynolds and Wynd,[111] the inhibition of fermentation by radiations between 3000 and 2500A is a specific effect independent of general injury to the cells. Von Euler and Swartz[112] believed the efficacy of ultraviolet light in accelerating the synthesis of organic phosphoric esters during fermentation to be doubtful, although the inorganic phosphate is decreased.

According to Keeser,[113] glucolysis of 0.1-per cent glucose solution in the presence of yeast cells was accelerated by irradiation with red light for thirty minutes, but white, green or blue light had little effect. Similar results were obtained with fructose, and also in the glucolysis of glucose or fructose by guinea pig serum. Irradiation of ox serum for five hours did not alter the reducing power or content of inorganic phosphorus of the serum, but ultraviolet irradiation increased the reducing power without altering the inorganic phosphorus.

The effect of carbon monoxide in inhibiting the anaerobic fermentation of tetanus or gas gangrene bacilli is increased by light, according to Schlayer.[114] Since only the combination of carbon monoxide with an iron compound is dissociated by light, the fermentation enzyme of these organisms must be an iron catalyst. In the case of an anaerobic butyric acid fermentation process, Kempner and Kubowitz[115] could demonstrate a similar phenomenon only at low temperatures and by the use of very great light intensities. Under these conditions, the fermentation can be completely and reversibly inhibited by carbon monoxide, light destroying the

[104] See also Söhngen, N. L., and Coolhaas, C., *Woch. Brau.*, **40**, 187 (1923); *Chem. Abs.*, **18**, 1030 (1924); Rennhard, A. W., *Compt. rend. soc. biol.*, **89**, 1080 (1923).

[105] De Fazi, R., *Ann. Chim. Applicata*, **4**, 301 (1915); **6**, 221 (1916); **8**, 93 (1917); *Chem. Abs.*, **10**, 950 (1916); *J. Ind. Eng. Chem.*, **13**, 265 (1921); *Atti R. Accad. Lincei*, **5**, 344, 901 (1927); *Brit. Chem. Abs.*, **A**, 592, 1113 (1927); *Chem. Abs.*, **21**, 2045 (1927).

[106] Sanzo, L., and Pirrone, F., *Atti Accad. Lincei*, **13**, 613 (1931); *Chem. Abs.*, **26**, 2990 (1932).

[107] Owen, W. L., and Mobley, R. L., *Zentr. Bakt. Parasitenk., Abt. II*, **88**, 273 (1933); *Chem. Abs.*, **27**, 5470 (1933); Owen, W. L., *Food Ind.*, **5**, 252 (1933); *Chem. Abs.*, **28**, 254 (1934).

[108] Beckwith, T. D., and Donovick, S. E., *Proc. Soc. Exptl. Biol. Med.*, **35**, 36 (1936).

[109] Marmeli, E., and Baratto, A., *Ann. chim. farm.*, No. 1, 18 (1938); *Chem. Abs.*, **32**, 6269 (1938).

[110] Tanner, F. W., *J. Ind. Eng. Chem.*, **13**, 265 (1921); *Chem. Gaz.*, **75**, 309 (1923); Tanner, F. W., and Byerley, J. R., *Arch. Microbiol.*, **5**, 349 (1934); *Chem. Abs.*, **28**, 5594 (1934).

[111] Reynolds, E. S., and Wynd, F. L., *Ann. Mo. Botan. Gardens*, **22**, 853 (1935); *Chem. Abs.*, **30**, 3855 (1936).

[112] von Euler, H., and Swartz, O., *Arkiv Kemi, Mineral. Geol.*, **9**, 21 (1925).

[113] Keeser, E., *Arch. Exptl. Path. Pharmakol.*, **170**, 500 (1933).

[114] Schlayer, C., *Biochem. Z.*, **276**, 460 (1935).

[115] Kempner, W., and Kubowitz, F., *Biochem. Z.*, **265**, 245 (1933).

inhibition. The light-sensitivity is very much smaller than in the case of the carbon monoxide combination with the enzyme concerned with respiration. The carbon monoxide compound of the enzyme concerned in the butyric acid fermentation absorbs within the special range 6500 to 3660A.

The action of photocatalysts in the fermentation of lactose by *Es. coli* is stimulating or inhibiting according to the quantity and quality of the catalyst.[116]

Molds. Reports on molds are conflicting. Some workers state that molds are killed by exposure to ultraviolet light without much difficulty.[117] Others report that molds are killed by ordinary exposure only when present in very small amounts. Some molds have protection in the form of fatty or waxy secretions. The latter may shield the mold from some radiations.

Fulton and Coblentz[118] exposed spores of 27 species of fungi for one minute to ultraviolet radiation from a mercury tungsten arc at a distance of six inches. There was complete killing of the spores of 16 species and a survival of less than 1 per cent in four species. It was hoped that this process could be applied to the killing of molds and fungi on oranges. Such a dosage caused no injury to the fruit. The limitation of the method, however, lies in the fact that the rays do not penetrate sufficiently beneath the surface to afford complete disinfection of the fruit.

Dillon-Weston[119] finds the spores of *Puccinia graminis tritici* to be killed more easily when irradiated in water than when irradiated dry. The white and orange specimens of certain physiological forms of the fungus are more susceptible than the red and gray ones. The pigments of the spore walls probably have some protective action. Sibilia[120] believed that ultraviolet rays activate the germination of the teleutospores of *Puccinia coronifera* of oats and *P. triticina* and to a lesser extent of *P. graminis*.

Smith[121] finds the death of *Fusarium* spores exposed to ultraviolet light at different temperatures to take the form of sigmoid curves which rapidly approach the logarithmic type as the temperature is increased. The average temperature coefficient between 0 and 40°C. is 1.13, but between 40 and 50°C. it is 1.37.

Johnson[122] finds rays in the Schumann region to be highly destructive to the upper layers of the mycelium of the fungi, *Collybia dryophila, Sclerotium batacicola,* and *Fusarium batacia.* The effect was localized and did not extend deeply into the culture. Ultraviolet rays passing through Vitaglass had a more injurious effect than those passing the Corning filter 980A. Those passing through Cellophane were intermediate in their action. According to Ramsey and Bailey,[123] irradiation by a quartz mercury arc stimulates spore formation in cultures of *Macrosporium tomato* and *Fusarium cepae.*[124]

Viruses and Bacteriophages. According to Baker and Nanavutty,[125] the bacteriophages are about as susceptible as the bacteria to irradiation, and the rela-

[116] Guerrini, G., *Boll. soc. ital. biol. sper.*, **10**, 847 (1935); *Chem. Abs.*, **30**, 8284 (1936).

[117] Houghton, E. M., and Davis, L., *Am. J. Public Health*, **4**, 224 (1914); Fairhall, L. T., and Bates, P. M., *The Cotton Oil Press*, 33 (1921).

[118] Fulton, H. R., and Coblentz, W. W., *J. Agr. Research*, **38**, 159 (1929).

[119] Dillon-Weston, W. A. R., *Sci. Agr.*, **12**, 81 (1931); *Chem. Abs.*, **26**, 497 (1932); Dillon-Weston, W. A. R., and Halnan, E. T., *Phytopathology*, **20**, 959 (1930); *Chem. Abs.*, **25**, 2233 (1931).

[120] Sibilia, C., *Boll. staz. patol. vegetale*, **11**, 115 (1931); *Chem. Abs.*, **26**, 1958 (1932).

[121] Smith, E., *Bull. Torrey Bot. Club*, **62**, 45 (1935); *Chem. Abs.*, **29**, 1130 (1935).

[122] Johnson, F. H., *Phytopathology*, **22**, 277 (1932).

[123] Ramsey, G. B., and Bailey, A. A., *Bot. Gaz.*, **89**, 113 (1930); *Chem. Abs.*, **24**, 3261 (1930).

[124] See Hutchinson, A. H., and Ashton, M. R., [*Canadian J. Research*, **3**, 187 (1930); *Chem. Abs.*, **25**, 315 (1931)] for the action of various mercury lines on the fungus, *Colletotrichum phomoides.*

[125] Baker, S. L., and Nanavutty, S. H., *Brit. J. Exp. Path.*, **10**, 45 (1929); see also Appelmans, R., *Arch. Intern. Pharmacodyn.*, **27**, 95 (1922); *Chem. Abs.*, **17**, 1978 (1923).

tive efficiencies of various spectral regions are about the same as for *B. coli*. Mizuno [126] found the destructive action to vary with the medium, being weak in broth, moderate in water and strongest on agar plates. Among the bacteriophages which have been affected by irradiation are those for *B. coli D*,[127] cholera, staphylococci, and dysentery.[128] The ultraviolet absorption of colon bacteriophages has been measured by Sandholzer, Mann and Berry.[129]

The work of Rivers and Gates [130] indicates that the susceptibility of vaccinia virus to irradiation is of the same order as that of bacteria. Galloway [131] finds the virus of foot-and-mouth disease to be destroyed after five minutes of exposure of filtrates to the radiations of a quartz mercury arc in quartz vessels. Also, the virus is inactivated after thirty minutes if the rays are filtered through Vitaglass. In ordinary glass there is no lethal action.

The tobacco mosaic disease virus is similarly inactivated,[132] unless it has penetrated plant tissue. Stanley [133] finds 0.5-per cent solutions of the crystallized protein of this virus to produce (when irradiated for eight hours by the unfiltered rays of a quartz mercury arc) an inactive protein which retains certain chemical and serological properties of the original. However, the protein no longer is capable of producing either the mosaic disease or a high molecular weight protein on inoculation into Turkish tobacco plants. Neither does it cause local lesions in *Nicotinea glutinosa*. The product may be crystallized from solution but the crystal is more opalescent and more readily denatured than before irradiation. Its x-ray diffraction pattern, isoelectric point and optical rotation are unchanged. No marked change in molecular weight occurs, although the homogeneity of the molecules is decreased. The serum of an animal previously injected with the irradiated product has a neutralizing effect on the original virus. The survival-ratios during irradiation follow a simple exponential curve, the rate of the inactivation depending upon the incident energy, according to Price and Gowen.[134] The absorption spectrum of the crystalline virus differs from that of other proteins in having its absorption maximum at 2650A.[135] This suggests that the compound is a nucleoprotein, and for this there is independent chemical evidence. This suggestion is interesting in that it points to the conclusion that viruses, which lie on the border between the living and the lifeless, appear to have nucleic acid as a component.

Other viruses found to be inactivated by ultraviolet rays include those of herpes and encephalitis,[136] influenza,[137] and crystalline tomato bushy stunt virus.[138]

It has been shown by Herzberg [139] that certain dyes can sensitize the vaccine virus to visible light. Only the thiazine, acridine and thioxanthone dyes were stated to have this property. At a dilution of one in a million, methylene blue and thiopyronin acted the most rapidly, sensitizing the virus within twenty to forty seconds. For exposures of an hour the acridine dyes were found to be

[126] Mizuno, K., *Japan. J. Med. Sci., Bact. & Parasit.*, **1**, 52 (1929); *Chem. Abs.*, **23**, 5485 (1929).
[127] McKinley, E. B., Fisher, R., and Holden, M., *Proc. Soc. Exptl. Biol. Med.*, **23**, 408 (1926).
[128] Levaditi, C., and Voet, J., *Compt. rend. soc. biol.*, **120**, 385 (1935); *Chem. Abs.*, **30**, 1084 (1936); see also Hallauer, C., *Z. Infektionskrankh.*, **117**, 18 (1935).
[129] Sandholzer, L. A., Mann, M., and Berry, G. P., *J. Bact.*, **33**, 17 (1937).
[130] Rivers, T. M., and Gates, F. L., *J. Exp. Med.*, **47**, 45 (1928).
[131] Galloway, I. A., *Brit. J. Exptl. Path.*, **9**, 326 (1928).
[132] Arthur, J. M., and Newell, J. M., *Am. J. Bot.*, **16**, 338 (1929); **15**, 623 (1928).
[133] Stanley, W. M., *Science*, **83**, 626 (1936).
[134] Price, W. C., and Gowen, J. W., *Phytopathology*, **27**, 267 (1937).
[135] Lavin, G. I., and Stanley, W. M., *J. Biol. Chem.*, **118**, 269 (1937).
[136] McKinley, E. B., Fisher, R., and Holden, M., *Proc. Soc. Exptl. Biol. Med.*, **23**, 408 (1926).
[137] Wells, W. F., and Brown, H. W., *Am. J. Hyg.*, **24**, 407 (1936).
[138] Bawden, F. C., and Pirie, N. W., *Brit. J. Exptl. Path.*, **19**, 251 (1938).
[139] Herzberg, K., *Z. Immunitäts*, **80**, 507 (1933); *Chem. Abs.*, **28**, 5126 (1934).

effective in the greatest dilutions, one in fifty million. It was pointed out that irradiation of rabbit skin by short wave-lengths after the application of active virus (within eight hours of the inoculation) reduced the number of pustules produced, but no effects could be observed if the irradiation was given after sixteen hours. After the injection of methylene blue intravenously, irradiation modified the infection even when given 24 hours after inoculation. With light of longer wave-lengths, no modification could be produced by irradiations made later than seven hours after the inoculation, even in the presence of the dye. The same effect was obtained with sunlight used 24 hours after inoculation as with the best source of ultraviolet light used 72 hours after inoculation.

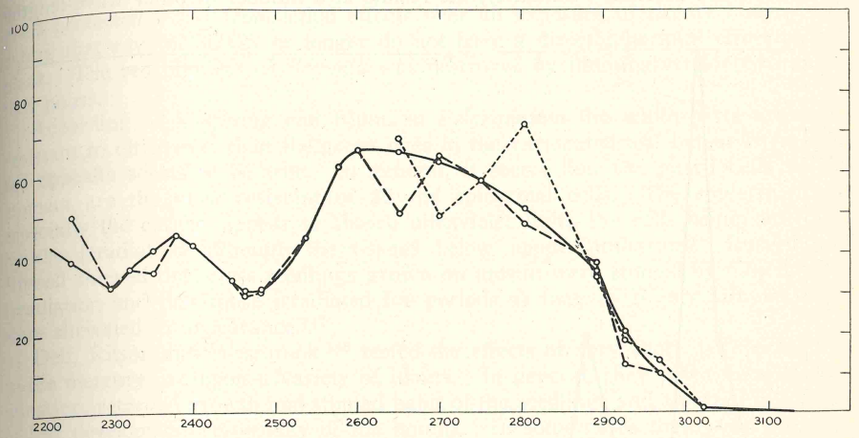


FIGURE 136. Radiotoxic Spectral Sensitivity of *Chlorella vulgaris* to Ultraviolet Rays. (From Meier, Smithsonian Miscellaneous Collections. The abscissae are wave-lengths in Ångstroms. The ordinates are relative lethal effectiveness in arbitrary units. Black line, smooth curve; dash line, actual values; dotted line, curve obtained by Meier, 1934).

Algae. Lami [140] found that ultraviolet irradiation of the alga, *Bonnemasonia asperagoides,* causes liberation of iodine from the gland cells. In the case of *Euglena,* Swann and del Rosario [141] found that in killing by α-particles, death was caused by a single impact with some sensitive entity of the cell, the size of which was about equal to that of the nucleus. In experiments with ultraviolet light, it appeared that the cells did not cease to die the moment irradiation was stopped, some cells apparently being affected in a manner which produced death some time later. Attempts were made to utilize absorption data on different parts of the cell to compute the volume of an assumed sensitive entity, on the assumption that the probability of reaction following absorption of a photon is unity. Attempts were also made to calculate the probability of killing on the basis that the volume of the assumed sensitive entity is that of the nucleus.

Meier [142] reported that the unicellular green alga, *Chlorella vulgaris,* is not killed by wave-lengths longer than 3022A. In subsequent work,[143] she irradiated

[140] Lami, R., *Compt. rend.*, **191**, 863 (1930).
[141] Swann, W. F. G., and del Rosario, C., *J. Franklin Inst.*, **213**, 549 (1932).
[142] Meier, F., *Smithsonian Misc. Coll.*, **87**, No. 10 (1932).
[143] Meier, F., *Ibid.*, **92**, No. 3 (1934); **95**, No. 2 (1936).

agar plates and inoculated them. As normal growth resulted, she concluded that radiations lethal to the organisms did not affect the medium in any way to accelerate or retard growth. She then made a number of exposures of plates (inoculated two to five months previously) behind a spectrograph for various periods from a few seconds to several hours and noted the regions in which decolorized areas became evident at intervals of from a few days to two months following irradiation. The lethal radiotoxic threshold for wave-lengths 2652 and 2804A lies between 100 and 120 seconds for intensities of 1960 and 1840 ergs per sq. cm. per second, respectively. Assuming the Bunsen-Roscoe law, for 1000 ergs per sq. cm. per second, the exposures required for 2652A would be 220 seconds and for 2804A, 206 seconds. Similarly, the results at a number of other wave-lengths

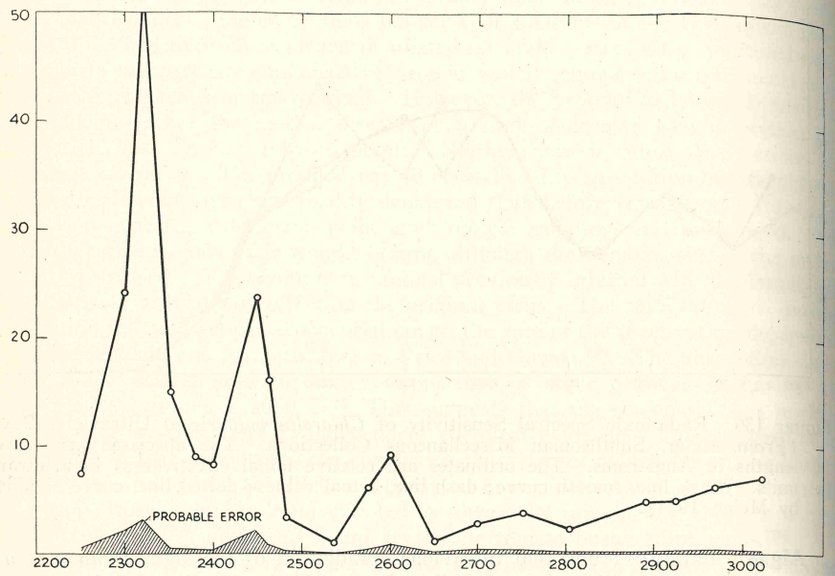


FIGURE 137. Radiotoxic Virulence Determined from *Chlorella vulgaris*. (From Meier, Smithsonian Miscellaneous Collections). The abscissae are wave-lengths in Ångstroms. The ordinates are radiotoxic virulence in arbitrary units.

were reduced to this common intensity and plotted in Figure 136 which shows a maximum lethal sensitivity at about 2600A. (Note similarity to the observations of Gates on bacteria.)[144] At the suggestion of Dr. C. G. Abbot, she introduced two new terms: radiotoxic spectral sensitivity and radiotoxic virulence. The former related to the certainty of the lethal action and the latter to the quickness of the attack. The distinction was drawn because death ensued much more quickly after irradiation in some spectral regions than in others. The data on the radiotoxic virulence are included in Figure 137 and show an alternate waxing and waning with decreasing wave-length and a high maximum at 2323A.[145]

[144] Note also Duggar, B. M., and Hollaender, A., *J. Bact.*, **27**, 219 (1934); Lucas, F., *Bell System Tech. Publ. Metallurgy Monogr.*, **B 792**, 1-47.

[145] For effects of portions of the visible and ultraviolet spectrum on cells of the prothallium of ferns, see Charlton, F. B., *Am. J. Botany*, **25**, 431 (1938).

Higher Plants. Hertel examined leaves of the aquatic plant *Elodea canadensis* under a microscope with a quartz condenser and illuminated with light of 2800A. The streaming movement of the granules in the living cells ceased almost immediately.

Work relating to the lethal effects of ultraviolet light on plant cells has been reviewed by Delf.[146] That single exposures may produce severe reactions was demonstrated by Maquenne and Demoussy in 1909, Kluyver in 1911, Ursprung and Blum in 1917, and Stoklasa in 1911. In Kluyver's experiment, exposures at 40 cm. from a mercury-vapor lamp for two and a half hours showed no immediate effects on leaves of *Aucubus*. Subsequently, however, the epidermal cells died, turning black in all leaves which had been exposed for forty minutes or longer. A cover glass protected a leaf from lethal effects over an exposure of twenty hours, indicating that rays of 3000A or longer do not have a directly harmful effect on the plant. The red pigment of *Begonia* was destroyed by illumination for two and a half hours.

According to Ursprung and Blum, in *Pelargonium* the white parts are more resistant to ultraviolet than the green ones in the variegated leaf but in *Vicia faba* the opposite seems to be true. In general, it seems that the guard cells of the stomata are the most resistant of all the epidermal cells. The epidermis, and especially the cuticle, appear to absorb ultraviolet light, the cells being destroyed by the irradiation although the tissues below appear unharmed. Russell and Russell showed that cress seedlings grown on muslin were stunted by mercury-arc irradiation and that those irradiated for periods as long as twenty minutes daily were shriveled in appearance.[147]

Delf, Ritson and Westbrook[148] tested the effects of very short daily exposures to the mercury arc upon a variety of plants. In general, they noted delayed germination, retarded growth and stunted habit of the seedlings and a partial inhibition of leaf development, especially of the lamina. In some cases there was a darker green color and in one case a loss of anthocyanin pigment in the lamina. With longer exposures, older plants showed a promoted leaf fall, and retardation of flower formation and of the opening of previously formed buds. In these cases the exposures were from two to ten minutes repeated from four to eight times daily. With exposures of thirty seconds or less the results were different. In one case, flowering of *Pelargonium* seemed to be promoted, in another the leaves of the irradiated plant ultimately surpassed those of the control in size; and in a third case, after a month of thirty-second daily irradiations at a distance of eight feet, there was a permanent and very favorable after effect in *Trifolium*. In the plant *Voandzeia*, exposures of five minutes daily led to definite anatomical changes during development, such as a reduction in the total thickness of lamina, development of more compact mesophyll with smaller and fewer air spaces, reduction in mechanical tissue and collapse of the cells of the upper epidermis followed by the withdrawal of the chloroplasts from the upper parts of the palisade cells. Martin and Westbrook[149] made histological examinations of leaves (*Pulmonaria* or *Aucuba*) at varying periods during irradiation. Lethal changes were first evident in the epidermal cells in the nuclei which coagulate, darken and become disorganized to one or more irregular masses. Later the cytoplasm becomes finely granular

[146] Delf, E. M., *Brit. J. Actinotherap.*, **2**, 106 (1927).

[147] Kluyver, A. J., *Sitzb. Math. Acad. Wiss., Wien.*, 120, 195 (1911); *Chem. Abs.*, **6**, 3108 (1912); Ursprung, A., and Blum, G., *Ber. Deut. Bot. Ges.*, **35**, 385 (1917); Russell, E. H., and Russell, W. K., "Ultraviolet Radiation and Actinotherapy," New York, Wm. Wood, 1925.

[148] Delf, E. M., Ritson, K., and Westbrook, A., *Brit. J. Exptl. Biol.*, **5**, 138 (1927).

[149] Martin, B. T., and Westbrook, M. A., *J. Exptl. Biol.*, **7**, 293 (1930).

and rapidly darkens. For small doses the reciprocal of the latent period for visible browning is proportional to the dose expressed in Clark lithopone units, but doses between ten and fifteen units make the latent period very short. During irradiation the temperature coefficient was about 1.1, but during the latent period it was higher, from 1.32 to 2.9.

Gilles,[150] states that the germination of lentil and turnip seeds is accelerated but their growth is somewhat retarded by mercury-arc irradiation.

Protozoa. There have been comparatively few investigations of the effects of ultraviolet light on amoebae.[151] Heilbrunn and Daugherty assumed that ultraviolet rays cause first a breakdown of a calcium gel in the cortex followed by the entry of this calcium into the interior where it produces a preliminary liquefaction followed by gelation. According to Black[152] media which favor motility tend to exert a synergistic action with the rays (2540A) in decreasing motility and producing cytolysis.

Paramecia have been studied under radiations. Hughes and Bovie[153] observed cytolysis in this organism under ultraviolet irradiation. Harris and Hoyt[154] employed paramecia in their work on the significance of the aromatic amino- acids to which allusion has been made. Bovie and Daland[155] found the short rays in the fluorite region to render *Paramecium caudatum* so sensitive to heat that amounts of heat insufficient to affect non-irradiated cells become lethal. Longer exposures to these rays caused death directly.[156] Bills[157] found that sunlight, but not indirect daylight, inactivates these organisms.

Weinstein[158] has given a curve (see Figure 134) for the relation between the wave-lengths used and the lethal action. It differs considerably from the analogous curves for bacteria in that the longer wave-lengths show greater effectiveness. In the case of such large cells there is some evidence to show that an optimum lethal action may occur closer to 2800A, the position of the maximum absorption by proteins, than to 2600A, that of the maximum absorption by nucleic acids. Leighton and Giese[159] have criticized the long wave-length limit indicated in the curve of Weinstein. They found that, although doses of only 16,500 ergs per sq. mm. sufficed to kill paramecia at 3025A within 24 hours after the irradiation, far greater dosages of the wave-length 3130A were ineffective. Doses as high as 191,000 to 200,00 ergs per sq. mm. had little if any effect. Weinstein had reported that the organism is killed about one-ninth as readily at 3130A as at 2654A and one-half as readily as at 3025A. Leighton and Giese attribute Weinstein's results to the presence of stray radiations, possibly the result of scattering within the quartz prism, in the light assumed to be of the wave-length 3130A. In general, Leighton and Giese found that to produce vesiculation (their criterion of death) in 50 per cent of the cells, a large number of quanta, 10^{13}, must be absorbed by each paramecium.

Hutchinson and Ashton[160] employed monochromatic light (both visible and

[150] Gilles, E., *Compt. rend. soc. biol.*, **109**, 739 (1932); *Chem. Abs.*, **27**, 3969 (1933).
[151] Folger, H. T., *J. Exp. Zool.*, **51**, 261 (1925); Heilbrunn, L. V., and Daugherty, K., *Protoplasma*, **18**, 596 (1933); *Chem. Abs.*, **27**, 4849 (1933).
[152] Black, W. A., *Univ. Calif. Pub. Zool.*, **41**, 75 (1936); *Chem. Abs.*, **30**, 8254 (1936).
[153] Hughes, D. M., and Bovie, W. T., *J. Med. Research*, **39**, 223, 233 (1918).
[154] Harris, F. I., and Hoyt, H. S., *Science*, **56**, 318 (1917).
[155] Bovie, W. T., and Daland, G. A., *Am. J. Physiol.*, **66**, 55 (1920).
[156] Forbes, H. S., and Daland, G. A., *Am. J. Physiol.*, **66**, 50 (1923).
[157] Bills, C. E., *Biol. Bull. Marine Biol. Lab.*, **47**, 253 (1924).
[158] Weinstein, I., *J. Opt. Soc. Am.*, **20**, 433 (1930).
[159] Leighton, P. A., and Giese, A. C., *J. Gen. Physiol.*, **18**, 557 (1934); *Science*, **81**, 53 (1935).
[160] Hutchinson, A. H., and Ashton, M. R., *Canadian J. Research*, **1**, 292 (1929).

ultraviolet), and in their controls took into account the period of the growth curve at which the specimens were taken. They believed that certain frequencies in the red, yellow and near ultraviolet regions stimulated growth, and the green rays as well as ultraviolet rays shorter than about 3000A retarded growth or killed the cells. Effects were different during the early and later portions of a 24-hour irradiation in some cases.

Alpatov and Nastyukova[161] find *Paramecium caudatum* twice as susceptible to the stimulating and depressing actions of radiations as *Paramecium bursaria*, which contains green symbiotic algae. After the latter had been kept in darkness until the algae lost their color, the two species were equally susceptible. The addition of electrolytes which induce swelling in colloids decreased the resistance of the organisms to ultraviolet rays and those which shrink colloids made the organisms more resistant.[162] Increase in viscosity produced by an electric current increased the resistance and decreases in viscosity produced by chloretone decreased resistance to irradiation.

A latent period of several minutes to hours between the cessation of irradiation of *P. bursaria* and the death of many cells has been emphasized by Tang and Gaw,[163] who have discussed the effects of the age of the organisms upon the constants of an empirical equation for the survival curve.[164] Tchakhotine,[165] by means of an ultramicroscope, observed the flocculation of cell colloids by the passage of a sharp pencil of ultraviolet light into the cytoplasm of amoebae, paramecia, spyrogyra and other organisms. Localized flocculations of cytoplasmic proteins cannot be obtained. Nuclear substances change in dispersion but do not precipitate.

Eggs, Embryos, Lower Animal Forms. The oöcysts of *Eimeria tenella*, if unsegmented, suffer a 100 per cent mortality after a ten-minute exposure to a temperature of 53°, 15 seconds at 60° or to three quarters of a zinc sulfide unit of ultraviolet light.[166]

Lillie and Baskerville[167] found that exposure of unfertilized eggs of *Arbacia* to ultraviolet light for five to fifteen minutes caused membrane formation and cytolysis. The treated eggs, unless overirradiated, showed the usual increased susceptibility to hypertonic sea water. Even when the radiations had been too weak to produce membranes, the susceptibility to hypertonic sea water was increased. Hinrichs[168] found that regions of high physiological activity were modified first in development by radiations. These regions were also the first to recover from slight injury. Irradiation of the sperm reduced its motility, delayed cleavage and interfered with the normal development of the zygote. Loose sperm suspensions of *Arbacia* lost their fertilizing power more rapidly on irradiation than concentrated ones. The sperm was agglutinated.

Klugh[169] used filters in comparing the effects of various components of sunlight on a series of seven marine organisms which differed widely in their response

[161] Alpatov, V. V., and Nastyukova, O. K., *Proc. Soc. Exp. Biol. Med.*, **32**, 99 (1934).
[162] Alpatov, V. V., and Nastyukova, O. K., *Compt. rend. Acad. Sci. U.R.S.S.*, **3**, 595 (1934); *Chem. Abs.*, **29**, 2182 (1935).
[163] Tang, P. S., and Gaw, H. Z., *Chinese J. Physiol.*, **11**, 305 (1937); *Chem. Abs.*, **31**, 4728 (1937).
[164] Early observations are due to Dreyer, G., *Mitt. Finsen's Lichtinstitut*, **4**, 81 (1903); **7**, 98 (1904); Hertel, E., *Z. Allgem. Physiol.*, **5**, 95 (1905); Sonne, C., *Arch. Phys. Therap. X-Ray, Radium*, **10**, 239 (1929).
[165] Tchakhotine, S., *Compt. rend.*, **200**, 2036 (1935); *Chem. Abs.*, **29**, 587 (1935); *Boll. soc. ital. biol. sper.*, **4**, 475 (1929); *Trans. Faraday Soc.*, **33**, 1068 (1937); *Compt. rend.*, **206**, 133 (1938).
[166] Fish, F., *Science*, **73**, 292 (1931); *Chem. Abs.*, **25**, 2771 (1931).
[167] Lillie, R. S., and Baskerville, M. L., *Am. J. Physiol.*, **61**, 272 (1922).
[168] Hinrichs, M., *Biol. Bull. Marine Biol. Lab.*, **50**, 55, 473 (1926).
[169] Klugh, A. B., *Canadian J. Research*, **1**, 100 (1929).

to light. It was concluded that there is a fairly close relation between the depth at which the organisms live and their susceptibility to radiations of shorter wave-lengths. In several cases lethal effects were found even though all the radiations used were present in sunlight.

Pigmented embryos of the nocturnal slug, *Limax flavus,* are easily injured by ultraviolet rays.[170] The deeply pigmented ones are especially sensitive.

The eggs and the first instar larva of the bean weevil, *Bruchus obtectus,* are killed by light of wave-lengths less than 3126A.[171] Adults showed no visible effects on irradiation, but most of their eggs were sterile. Sublethal doses produced weevils defective in metabolic processes.

Stevens[172] found that total arc exposure of the whole *Ascaris* egg for six or eight hours usually did not kill the egg at once, but prevented further development if the eggs had been in the two-cell or four-cell stage at the time of exposure. With shorter exposures, there was observed irregular fragmentation of the chromosomes, delay in cleavage and abnormal gastrulation. Schleip[173] irradiated various parts of the egg separately and concluded that no one part could be affected without producing some alteration in the unirradiated parts as well. Ruppert[174] found a rhythmic alteration in the lethal effect, depending on the stage of development of the egg when irradiated with energy of a wave-length of 2800A.[175]

Wright and McAlister[176] found ova of the roundworm of the dog, *Toxascaris Leonina,* to exhibit retarded embryonation after irradiation with the lines 2652 or 2804A at intensities of 684,000 ergs per sq. cm. They were particularly interested in the possible lethal action of sunlight, but found destructive effects only with the wave-length 3022A, but not with longer ones. Even at 3020A, 137,000,000 ergs per sq. cm., approximately equivalent to twelve days of July sunlight at Washington, D. C., caused only 1.5 per cent of the ova to reach embryonation, as compared with 42 per cent in the controls. For *Toxocara* ova, the corresponding figures were 20.5 per cent as compared with 65.5 per cent. The lesser susceptibility of this species may be due to absorption or dispersion of the light by the mosaically patterned, darkly pigmented shell of these eggs as compared with the clear, lightly pigmented shell of the *Toxascaris* ova. The ultraviolet rays of sunlight may be a factor, along with temperature and desiccation, in the marked lethal action of sunlight on ova reported by several workers.

Applications

The Sterilization of Water. At one time sterilization by ultraviolet bid fair to be the method of choice for the treatment of water on a large scale and several installations were claimed to have been satisfactory. A description of the operation of an installation at Henderson, Ky., given by Smith,[177] states that there was little or no variation in the results, the rate of pumping being 2,200,000 to 3,200,000 gallons per day. The energy expenditure was said to have been 92.5 kilowatt hours per million gallons.

[170] Carmichael, E. B., *Physiol. Zool.,* **4,** 575 (1931).
[171] MacLeod, G. F., *Ann. Entomol. Soc. Am.,* **26,** 603 (1933).
[172] Stevens, N. M., *Arch. Entwicklungsmech. der Organismen,* **27,** 622 (1909).
[173] Schleip, W., *Arch. Zellforsch.,* **17,** 289 (1923).
[174] Ruppert, W., *Z. wiss. Zool.,* **123,** 103 (1924).
[175] Note also Seide, J., *Z. wiss. Zool.,* **124,** 252 (1925); *Chem. Abs.,* **20,** 1871 (1926); Nolf, L. O., *Am. J. Hyg.,* **16,** 288 (1932).
[176] Wright, W. H., and McAlister, E. D., *Smithsonian Misc. Coll.,* **93,** 1 (1934).
[177] Smith, A. T., *Eng. News Record,* 1021 (1917).

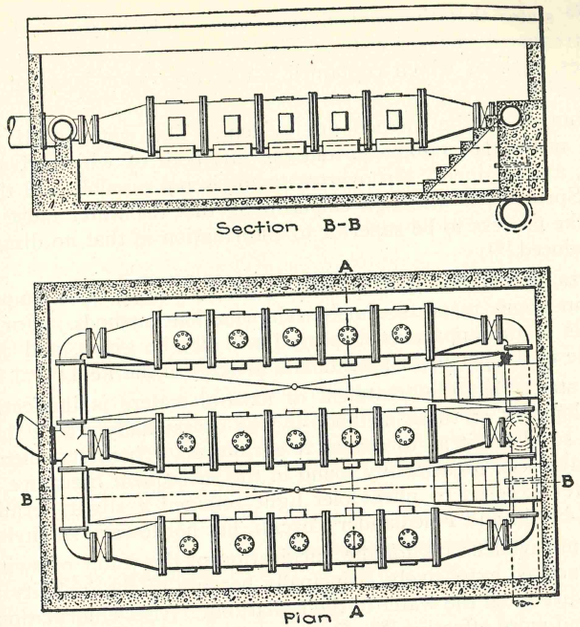


Figure 138. Large-scale Water Sterilization Equipment.

The ultraviolet sterilizers consisted of three legs each comprising five units. (Figure 138.) The legs were connected in parallel and the entire equipment was connected in series with a pipe line leading from the filtered water basin to the storage for the city supply. Each unit had a lamp box inserted in the side equipped with a clear quartz closed-end tube which projected into the body of the unit and around which the water was forced in a thin film by means of a baffle placed at 90° to the long axis of the sterilizer. The quartz tube was contained in a slotted opening in the baffle. (Figure 139.) The lamp

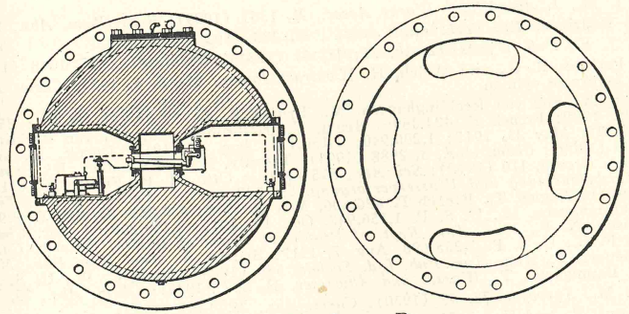


Figure 139. Lamp Box.

proper was a 220-volt d.c. mercury arc designed to be automatically tilted for starting by a special support located in the lamp box. The individual lamps were so connected that they could be adjusted individually. They were also connected to the main switchboard, each lamp having an incandescent lamp and a warning bell to notify the operator of improper operation.

Blocher [178] states that the method was successfully in use at Berea, Ohio, in 1929 for the treatment of river water. The water was passed through four copper boxes in series, each of which contained a mercury-vapor lamp surrounded by a quartz cylinder.[179]

The advantages of the method are evident. The water itself undergoes no change. The materials in solution and the air, both of which give the water a pleasant taste, are retained. An overtreatment is not possible and the cost is not prohibitive. Springer,[180] although emphasizing that the water must first be clarified, believes the process to be superior to chlorination in that no disagreeable odor or taste is produced.[181]

Nevertheless, the method has declined in favor owing to the competition of the cheaper and in some respects simpler chlorination methods. For this reason working details of the apparatus employed will not be given, and reference will merely be made to the pertinent patents and articles in the field.[182]

Beattie [183] states that the treatment of natural waters is ineffective. During the early development of these methods it was occasionally stated that the treatment of water so alters it as to render it germicidal. Such statements were disputed,[184] but have been occasionally found in the subsequent literature. Norton [185] stated that water exposed to ultraviolet light retained a slight germicidal power toward typhoid bacilli and Friedländer's bacilli, but not toward staphylococci.

The use of ultraviolet rays for the purification of the water of swimming pools is no longer practiced extensively, principally because of the inability to make the necessary exposure of all the water to the radiations. Also, chlorination is reported to be cheaper and more effective.[186] Occasionally a favorable report of the method still appears.[187]

There are, however, several fields in which the method is useful because the chemical methods may be objectionable and an overdose harmful. Among these are the sterilization of water for surgical purposes under certain conditions, the sterilization of bottled waters, and other beverages (before bottling),[188] and the treatment of water intended for washing butter and for use in foods.[189]

Lloyd [190] claims that the exposure of filtered sea water to ultraviolet light for one second sterilizes it effectively. The cost of irradiation treatment is said to be about a hundred times that of chlorination.[191]

Residual chlorine and chloramine in distilled water drop markedly on exposure of the water to arc lamps, and the acidity increases in proportion to the reduction in free chlorine.[192] The *o*-tolidine reagent used in the free chlorine test becomes unreliable because of discoloration after exposure to direct sunlight for two months. Similar discoloration impairs the dichromate-copper sulfate standard.[193]

[178] Blocher, J. M., *J. Am. Water Works Assoc.*, **21**, 1361 (1929); *Brit. Chem. Abs.*, **1929B**, 1034.

[179] Note also Rodriguez-Ely, *Tech. sanit. munic.*, **30**, 288 (1935).

[180] Springer, J. F., *Pub. Works*, **62**, 10, 36; **11**, 65 (1931); *Chem. Abs.*, **26**, 1048 (1932).

[181] See also Perkins, R. G., and Welch, H. [*Contract Journ.*, March 4, 1931; *Chem. Abs.*, **26**, 1997 (1932)] for a favorable opinion.

[182] Helbronner, A., and von Recklinghausen, M., British P. 4,895; 24,632; 28,067; 25,883; 21,829; 30,397, Dec. 29, 1909; French P. 424,369. Henri, V., Helbronner, A., and von Recklinghausen, M., U. S. P. 1,140,819, May 25, 1915; 1,200,940; 1,150,117, Aug. 17, 1915; Dornic, P., and Daire, P., *Chem. Ztg.*, 936 (1909); *Chem. Abs.*, **3**, 2988 (1909); Tassilly, E., and Cambier, R., *Compt. rend.*, **151**, 342 (1910); *Eng. Record*, 110 (1912); *Sci. Am.*, 515 (1917); Otto, M. P., French P., 421,296, Oct. 10, 1910; *J. für Gasbeleuchtung und Wasserversorgung*, **56**, 528 (1913); Perkin, F. M., *Trans. Faraday Soc.*, **6**, 199 (1911); Nogier, T., French P. 426,606, May 6, 1910; 420,281; British P. 9,960, April 20, 1911; von Recklinghausen, M., U. S. P. 1,156,947, Oct. 19, 1915; 1,193,209; *J. Soc. Chem. Ind.*, 976 (1916); Parkinson, N. F., *23rd. Ann. Rept. of Provincial Board of Health, Ontario, Canada*, **33**, 156 (1914); Keyes, F. G., U. S. P. 1,235,698, Aug. 7, 1917; Bruére, S., *Ann. Hyg. Pub., New Series*, **1**, 348 (1923); Dienert, F., *Ann. Hyg. Pub. Ind. Sociale*, 586 (1924); Sirch, C. W., U. S. P. 1,860,435, May 31, 1932; Baumgärtel, T., *Wasser und Abwasser*, **33**, 207 (1935); *Chem. Abs.*, **29**, 6677 (1935).

[183] Beattie, J. M., *Surveyor*, **78**, 69 (1930); *Chem. Abs.*, **26**, 1365 (1932).

[184] Cernovodeanu, P., and Henri, V., *Compt. rend.*, **150**, 52 (1910).

[185] Norton, J. F., *Am. J. Pub. Health*, **18**, 476 (1928); Vadimov, M., *Priroda*, **24**, No. 4, 13 (1935); *Chem. Abs.*, **31**, 7074 (1937).

[186] See Heath, R. F., *Can. Engr.*, **70**, No. 14, 27 (1936); *Chem. Abs.*, **30**, 7746 (1936).

[187] Turner, A. A., *J. Roy. Sanit. Inst.*, **55**, 441 (1935); *Chem. Abs.*, **30**, 1481 (1936).

[188] Schnegg, H., Kipphan, H., and Grunert, K., [*Z. ges. Brauw.*, **59**, 21 (1936); *Chem. Abs.*, **30**, 8513 (1936)] discuss its use in breweries.

[189] Stateler, E. S., *Food Ind.*, **7**, 535 (1935).

Sterilization of Food Products

Sterilization of Milk and Other Opaque Substances. After the introduction of ultraviolet sterilization, many patents describing processes for treating milk were issued. These will not be described in detail since the process apparently interferes with the irradiation of milk for the production of vitamin D, and because complete sterilization is difficult. Also the prolonged treatment necessary for sterilization is reported to have deleterious effects upon the flavor of the milk.[194] In the patent of Henri and von Recklinghausen, it was stated that heating the milk to 60°C. before irradiation would make the bacteria more sensitive to the action of the rays. In addition to the preheater (Figure 140) there was employed a rotating

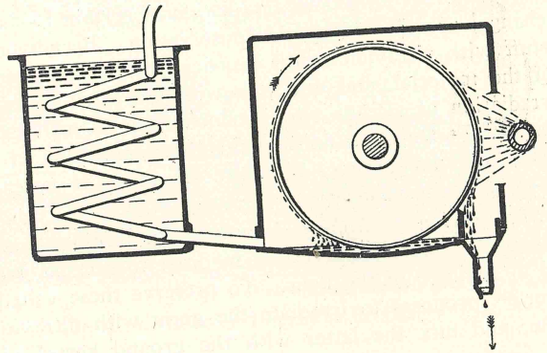


FIGURE 140. Apparatus of Helbronner and von Recklinghausen for Heat and Ultraviolet Treatment of Milk.

drum to pick up a very thin film of the milk, a procedure frequently used in irradiation of opaque fluids. von Recklinghausen [195] obtained a thin film by passing the liquid between two plates, one of quartz, the plates being separated by sheets of tin foil. Further patents dealt with details of methods for removing milk from rotating drums or rollers in such a manner as to avoid formation of particles of butter on the roller.[196]

[190] Lloyd, B., *J. Roy. Tech. Coll.*, **3**, 505 (1935); *Chem. Abs.*, **29**, 4041 (1935).

[191] Vagedes, H., *Gas-und Wasserfach*, **78**, 80 (1935); *Chem. Abs.*, **32**, 1826 (1938).

[192] Buchanan, E. B., and Dodge, J. K., *15th Ann. Rept. Ohio Conf. Water Purif.*, 40 (1936); *Chem. Abs.*, **30**, 6859 (1936).

[193] Davis, W. S., and Kelly, C. B., *J. Am. Waterworks Assoc.*, **26**, 757 (1934); *Chem. Abs.*, **28**, 4807 (1934).

[194] Henri, V., and von Recklinghausen, M., U. S. P. 1,141,046, May 25, 1915.

[195] von Recklinghausen, M., U. S. P. 1,165,921, Dec. 28, 1915; *Chem. Abs.*, **10**, 649 (1916).

[196] Henri, V., Helbronner, A., and von Recklinghausen, M., U. S. P. 1,140,818, May 25, 1925; 1,068,898, July 29, 1913; 1,052,818, Feb. 11, 1913; Helbronner, A., and von Recklinghausen, M., British P. 12,948, May 27, 1910; 18,458, Aug. 4, 1910; for sterilizing fats and butter, note Soc. Le Serment, French P. 400,921, March 17, 1909.

Potencier [197] delivers milk under carbon dioxide pressure from a tank onto a metal or transparent table in a thin layer and collects the milk in a gutter surrounding the table. The rays are emitted from tubes situated under a parabolic cupola above the table. The cupola may be made either of polished metal or of insulating material faced on the inside with a fluorescent coating yielding rays between 2300 and 4500A. Scheidt [198] used a lamp in which a high-tension discharge is passed through neon and argon in a series of quartz tubes either U-shaped or formed of two coaxial vertical rims one enclosing the other. The rays are allowed to act on the liquid as it flows in a thin film between the surfaces of the quartz tubes and surrounding tubes of porcelain.

Vogeler [199] states that sterilization of milk by ultraviolet light is not a feasible process. Various attempts have been made to combine the use of ultraviolet rays with chemical treatments, using for example, hydrogen peroxide [200] or chlorine.[201]

Food Products.[202] The ingredients of jams, jellies, and other preserves may be subjected to the action of ultraviolet rays while being heated in a shallow pan provided with means for agitation and removal of the scum.[203] Perino [204] suggested that nutritive extracts of vegetables be irradiated in the absence of oxygen.

Spolverini [205] states that ultraviolet irradiation of certain foods causes physical and chemical changes which tend to aid conservation. Berndt and Creighton [206] treat the foodstuff with ultraviolet until beneficial properties have been imparted to a portion of the material, and mix this with untreated material. Apparatus designed for irradiation of viscous food products such as malt extracts has been described by Rohde.[207] Duret [208] finds ultraviolet sterilization of sugar solutions of value because occasional samples of sugar are found to contain thermophilic bacteria which resist heat sterilization.

Ultraviolet Sterilization in Baking Industry. In milling flour, it is usually necessary to remove the germ from cereals in order to prevent growth of organisms which lead to spoilage of the flour. To preserve these valuable portions of the grain, Mayor [209] proposes to irradiate the germ with ultraviolet rays, roast the treated germ, and mix the latter with the ground kernel of the same or other cereal.

In the bleaching of flour, mercury-arc irradiation is occasionally employed to supplement the action of such bleaching agents as dibenzoyl peroxide. By this means it is said to be possible to obtain in one hour the amount of bleaching that

[197] Potencier, R., British P. 430,908, Dec. 21, 1933; *Brit. Chem. Abs.*, **B**, 827 (1935).

[198] Scheidt, E. O., British P. 257,956, Sept. 6, 1926; *Brit. Chem. Abs.*, **B**, 106 (1928); U. S. P. 1,670,217, May 15, 1928.

[199] Vogeler, L., *Milchwirtschaft Literaturber.*, 484 (1930); *Chem. Abs.*, **26**, 1039 (1932).

[200] Bing, M., German P. 392,935, 1922; *Brit. Chem. Abs.*, **B**, 345 (1927).

[201] Tranin, S., and Snyder, R. M., U. S. P. 1,945,102, Jan. 30, 1934; *Chem. Abs.*, **28**, 2428 (1934). Note for another recent milk patent, Castelain, L., U. S. P. 1,956,667, May 1, 1934.

[202] See Haines, R. B., Lea, C. H., Lea, D. E., and Tompkins, R. G., *Rep. Food Invest. Bd.*, 29, 1936; *Brit. Chem. Abs.*, **B**, 1264 (1937).

[203] McKinlay, D., British P. 273,578, Dec. 14, 1926; 272,775 (for fruits); *cf.* Mayor, J., U. S. P. 1,911,913.

[204] Perino, J., British P. 279,487, Oct. 22, 1926; *Chem. Abs.*, **22**, 2799 (1928).

[205] Spolverini, L. M., *Riv. ital. actionol.*, **2**, 1 (1927); *Chem. Abs.*, **23**, 4508 (1929).

[206] Berndt, E. C., and Creighton, H. M., U. S. P. 2,072,416-7-8; *Chem. Abs.*, **31**, 2701 (1937).

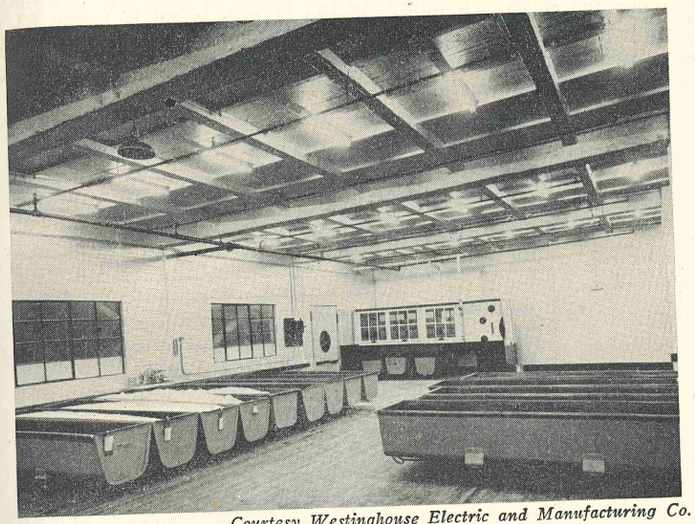
[207] Rohde, H. W., U. S. P. 1,888,472, to Jos. Schlitz Beverage Co.

[208] Duret, G., French P. 736,254, Aug. 13, 1931; *Chem. Abs.* **27**, 1540 (1933); British P. 395,527, July 20, 1933; *Chem. Abs.*, **28**, 362 (1934).

[209] Mayor, J., French P. 752,261, Sept. 20, 1933; *Chem. Abs.*, **28**, 838 (1934).

would be effected by allowing the peroxide to stand alone in contact with flour for 48 hours.[210]

Read [211] studied the use of various sources of ultraviolet light in killing mold spores infecting the surface of freshly baked bread. He did not find the mercury-vapor arc to offer the advantages to be obtained by the use of the carbon arc. With various carbons, the fungicidal potency decreases in the following order: "C," "U," "K" and Mg. On the other hand it has been stated that growth of molds in bread can be checked by utilization of discharge lamps containing argon, neon and mercury.[212] Rooms in which dough is stored for yeast reaction are kept



Courtesy Westinghouse Electric and Manufacturing Co.

FIGURE 141. Use of Ultraviolet Radiation in Dough Room of a Bakery.

warm and moist and these conditions favor the growth of molds. It was reported that such growth could be inhibited by exposing dough to lamps emitting radiation between 2000-2600A. The rays were said not to penetrate beneath the surface of the dough, and to have no effect upon the yeasting process (Figure 141). Also, lamps which furnish rays in the range mentioned have been employed in the cooling and wrapping rooms of bakeries to prevent deposition of bacteria on bread subsequent to the baking process. Bonsor [213] subjected the dough ingredients during mixing to ultraviolet light for five or ten minutes to render the final product lighter and more easily digested.

[210] Ferrari, C. G., and Croze, A. B., *Cereal Chem.*, **11**, 505 (1934); *Chem. Abs.*, **29**, 236 (1935); Ferrari, C. G., Croze, A. B., and Bailey, C. H., *Cereal Chem.*, **9**, 491 (1932); *Chem. Abs.*, **26**, 6027 (1932); Sutherland, E. C., U. S. P. 1,539,701, May 26, 1925; *Chem. Abs.*, **19**, 2246 (1925); British P. 249,139, March 11, 1925; 102,967, Dec. 22, 1915; *Chem. Abs.*, **11**, 1219 (1917); U. S. P. 1,381,079, June 7, 1921; 1,380,334, May 31, 1921; *Chem. Abs.*, **15**, 3349 (1921); Gelissen, H., U. S. P. 1.483,546, Feb. 12, 1924; *Chem. Abs.*, **18**, 1167 (1924). In the earlier patents, other oxidizing agents, usually peroxides, were suggested.

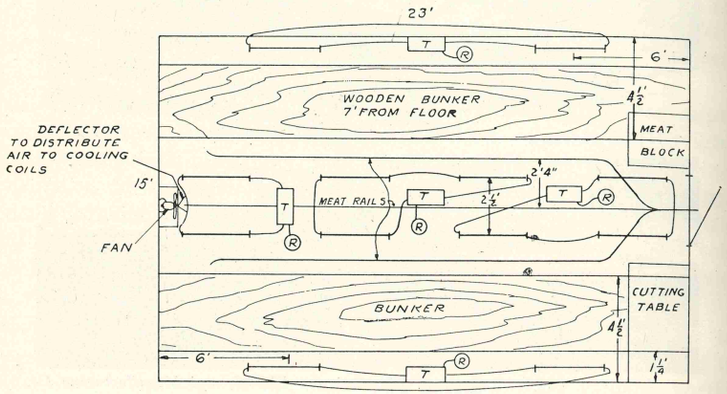
[211] Read, J. W., *Cereal Chem.*, **11**, 80 (1934); *Chem. Abs.*, **28**, 3142 (1934).

[212] Hibben, S. G., and Blackburn, P. W., *Electrical Engineering*, 455 (1938). Garrett, O. F., and Arnold, R. B., *Milk Plant Monthly*, August (1938). *Food Industries*, **10**, (5), 263 (1938). James, R. F., *Food Industries*, **10** (6), 295 (1936). Dennington, A. R., *The Bakers Technical Digest*, March (1937). Broadbent, H. S., *Food Industries*, **10** (6) (1938).

[213] Bonsor, S., British P. 280,729, Dec. 16, 1926; *Brit. Chem. Abs.*, **B**, 106 (1928).

Ultraviolet Sterilization in Meat Industry.[214] Freshly slaughtered beef is composed of small muscle fibers 0.002 inch in diameter and 1 to 2 inches in length enclosed in a sheath-like covering. The muscle fibers are bound together into larger aggregates by connective tissue. When beef is stored, the connective tissue is changed to a gelatin by enzymic action within the meat. This process, called tendering, may be accelerated by increasing the temperature. However, temperatures above refrigeration limit (above 45°F.) also speed up mold formation on the surface of the meat, thereby causing considerable loss of the latter when the mold is cut away.

Also, storing of meat may result in considerable shrinkage by evaporation of moisture when the relative humidity of the storage room is below 83 per cent. A relative humidity of 85-90 per cent in the vicinity of stored meat was stated to prevent evaporation from meat to a large extent. These highly moist conditions tend to accelerate mold formation.



Courtesy Westinghouse Electric and Manufacturing Co.

FIGURE 142. Use of Ultraviolet Lamps in Meat Storage Rooms.

The presence in a storage room of rays of about 2000-2600A was advocated as effective in inhibiting mold formations on meat surfaces, at temperatures above 35°F. and relative humidity of 85-90 per cent.[215] Lamps emitting these radiations generally are placed in rows parallel to the racks or rails on which meat is hung for storage or tendering (Figure 142). Also, it is reported that circulation of air in the storage room prevents mold formation in areas where meat is not exposed directly to rays from discharge lamps.

Miscellaneous Applications. Ultraviolet sterilization has been proposed as efficient for destroying bacteria on eating and drinking implements.[216] Exposure of glasses (after washing and rinsing) to rays from discharge lamps was reported to result in destruction of 87-100 per cent of the bacteria present.

[214] Ewell, A. W., *Refrigerating Engineering,* January (1939). Coulter, M. D., Address at Mellon Institute of Industrial Research, March 21, 1939. British P. 22,669, 1914, to Monvoisin, Barrat et Robin; *Chem. Abs.,* **10,** 1238 (1916).

[215] Lamps utilized for this purpose are known as Sterilamps (Trade Mark Registered U. S. Patent Office), manufactured by Westinghouse Electric & Manufacturing Co.

[216] R. V. Fellers, *The American City,* August, 53 (1938).

In the sterilization of fruit juices, Welch and Perkins[217] suggested the use of the photosensitizing action of eosin or fluorescein, only very small concentrations being required.

The condition of pitched barrels or casks is reported to be greatly improved, even though complete sterilization is not attained, by lowering quartz lamps into them and irradiating them for fifteen to thirty seconds. Longer periods may heat the casks to such an extent as to cause the liberation of the fumes of pitch.[218]

Sterilization of Medicinal Products

Vaccines. It was early proposed to treat vaccinia virus by ultraviolet rays, the belief being that harmful foreign organisms could be killed by doses insufficient to destroy the more resistant virus.[219] Kirstein,[220] using the Vitaray apparatus,

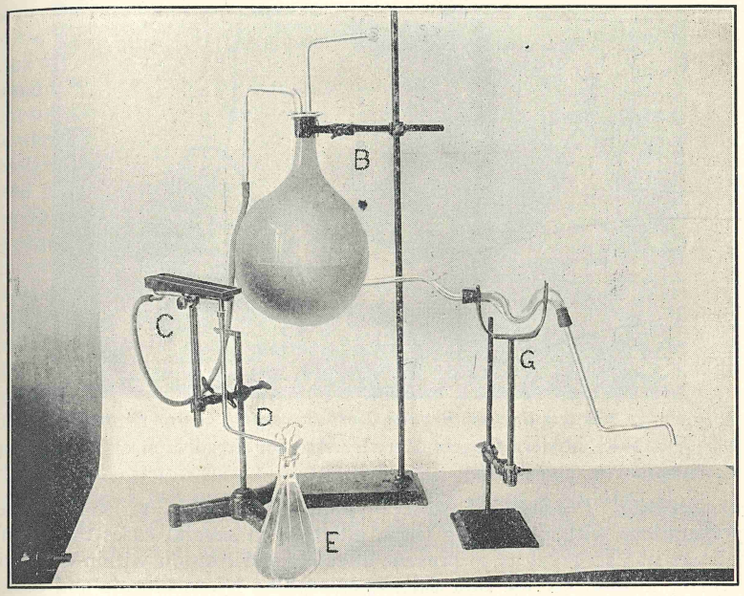


FIGURE 143. Apparatus of Hougton and Davis for Sterilization of Vaccines.

was unable to find any evidence of such action. Later, however, he introduced a process using a salicylic acid filter, which he claimed accomplished this purpose not in the case of the vaccinia virus, but in the preparation of various bacterial vaccines. The killing of the organisms was said to be accomplished by filtered ultraviolet rays.[221]

[217] Welch, H., and Perkins, R. G., *J. Prev. Med.,* **5,** 173 (1931); *Chem. Abs.,* **26,** 5362 (1932).

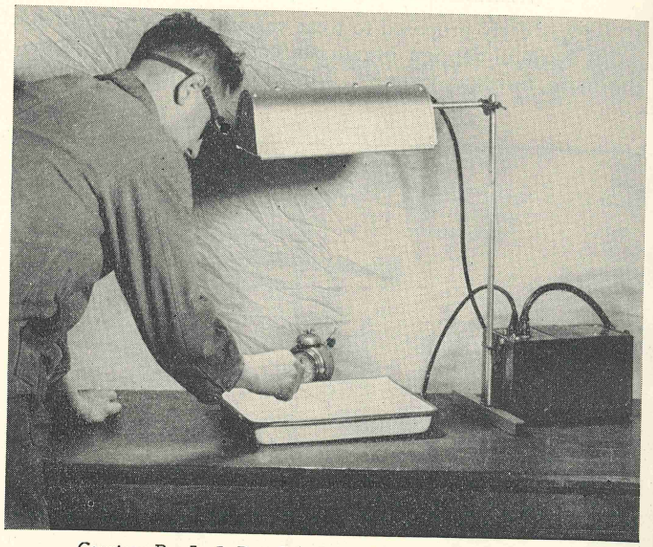
[218] *Sci. Am.,* 201, Aug. 28, 1920; Moufang, E., *Allgem. Z. Bierbrau Malzfab.,* **43,** 151 (1915).

[219] German P. 314,858, Feb. 24, 1914, to Quarzlampen Ges. Hanau; *J. Soc. Chem. Ind.,* **39,** 312 (1920); Friedberger, E., and Mironescu, E., *Deut. Med. Wochschr.,* 1203 (1914); Mayerhofer, E., *Z. Kinderheilk.,* **13,** 361 (1916).

[220] Kirstein, F., *Zentralb. Bakt. Parasitenk. Infektionsk.,* **I, 114,** 530 (1929).

[221] Kirstein, F., German P. 598,680, June 15, 1934; *Chem. Abs.,* **28,** 5932 (1934); German P. 600,941, Aug. 3, 1934; *Chem. Abs.,* **28,** 7433 (1934); German P. 609,258, Feb. 11, 1935; *Chem. Abs.,* **29,** 6366 (1935). Note also Mayer, G., German P. 505,707, April 3, 1927; *Chem. Abs.,* **25,** 382 (1931).

Figure 143 illustrates apparatus used by Houghton and Davis [222] for sterilizing bacterial vaccines and other products. The material to be irradiated is contained in a glass flask B connected by a sterile glass siphon and rubber tubing to the trough C placed directly beneath the arc. After exposure in the trough, the liquid passes through the delivery tube D into a previously sterilized container E. A modern quartz mercury arc suitable for irradiating the liquid in the trough is shown in Figure 144.



Courtesy Dr. L. J. Buttolph, Lamp Department, General Electric Co.

FIGURE 144. Modern Quartz Mercury Arc for Irradiation of Liquids.

Pharmaceutical Products. Lesure [223] found it possible to sterilize several drug preparations without altering them, although in several cases the absorption by the drugs was so great as to prevent effective sterilization within a reasonable time. Silver nitrate, eserine salicylate, apomorphine hydrochloride and atoxyl all became colored after five minutes of exposure and morphine hydrochloride, arbutin and guaiacol cacodylate after fifteen to thirty minutes. Arbutin became colored after three hours because of the formation of quinol and its oxidation products.

Sperti, Norris, Withrow and Schneider [224] proposed to employ only selected radiations, obtained by the use of filters of, for example, lead acetate, in destroying bacteria in enzyme solutions without affecting the enzyme activity. They also suggested that selective irradiation might be employed for activation of vitamins and for differentially affecting organic substances having several ingredients.

Mingoia [225] found it impossible to sterilize solutions of such alkaloids as heroine, cocaine, atropine and codeine by irradiation so as to render them suitable for hypo-

[222] Houghton, E. M., and Davis, L., *Am. J. Public Health*, **4**, 224 (1914).
[223] Lesure, A., *J. pharm. chim.*, **1**, 569 (1910); *J. Chem. Soc.*, **98**, 739 (1910).
[224] Sperti, G., Norris, R. J., Withrow, R., and Schneider, H., U. S. P. 1,676,579, July 10, 1928.
[225] Mingoia, Q., *Ann. chim. applicata*, **23**, 318 (1933); *Chem. Abs.*, **27**, 5889 (1933).

dermic use without at the same time altering the alkaloids seriously. Nitzescu [226] believed that insulin solutions could be sterilized in this manner.[227]

Kelly [228] proposed the sterilization by irradiation of certain emulsions used in ointments and shaving creams.

In treating substances serving as sources of essential oils, Tival and Descombes [229] first froze the material, then irradiated it and dried it *in vacuo* before extracting the oil. Rousseau [230] added uranium, iron or manganous salts to enzymes or yeast before subjecting the latter to the action of ultraviolet rays.

According to Stevens,[231] ultraviolet light renders the lipids of skin, extracted and emulsified in salt solution, bactericidal to hemolytic streptococci. It increases markedly the active oxygen content of dried skin, unless the lipids had been extracted before irradiation.

Various Products. Wool which has been treated with ultraviolet light is said [232] to have increased susceptibility to mold growth. Gelatin solutions and articles made from them, such as threads, cords, violin strings, ribbons, or tubes, may be sterilized by ultraviolet light, according to Hirsch.[233] Redd [234] describes apparatus for subjecting clothes to ultraviolet rays and ozone in laundry apparatus.

Lehmann [235] finds that staphylococci in contact with linoleum die more rapidly under strong illumination than when irradiated on glass or wood. This is ascribed to the action of oxidation products of the linseed oil present in the linoleum.

Considerable attention has recently been devoted to the bactericidal properties of irradiated petrolatum. Eising [236] noted that the latter exerted a strong bactericidal action upon the ordinary organisms of wound infection and believed it also to stimulate the processes of healing. Sheard and Thompson [237] found irradiated mineral oil less active than irradiated olive oil or Vaseline. Harris, Bunker and Milas [238] found the vapors of certain oils to inhibit or kill bacterial smears on nutrient agar without irradiation, although other oils acquired this power only after being irradiated. They believed the germicidal action due probably to volatile substances containing peroxidic oxygen in the oil, the formation of which is accelerated by irradiation, the most effective rays being about 3130A. In general, animal oils were more active than vegetable oils. The germicidal properties are not the result of secondary radiations, aldehydes, butyric acid or ozone. Sears and Black [239] observed that white petrolatum becomes germicidal after four hours of irradiation and changes to a limpid yellow color. The germicidal agent is believed to be a non-volatile chemical substance, not water-soluble, formed as the result of oxidation. It does not kill spores or certain gram-negative intestinal organisms. Stevens [240]

[226] Nitzescu, I. I., *Klin. Wochschr.*, **3**, 2343 (1924); *Chem. Abs.*, **19**, 1285 (1925).
[227] See, however, Chapter 34.
[228] Kelly, T. D., British P. 283,711, Dec. 13, 1926; *Chem. Abs.*, **22**, 4205 (1928).
[229] Tival, H., and Descombes, F., British P. 179,164, April 25, 1922; *Chem. Abs.*, **19**, 1019 (1925).
[230] Rousseau, E. F., British P. 226,534, Dec. 17, 1923; *Chem. Abs.*, **19**, 2103 (1925).
[231] Stevens, F. A., *J. Exptl. Med.*, **65**, 121 (1937).
[232] Burgess, R., *J. Soc., Dyers Colourists*, **50**, 138 (1934); *Chem. Abs.*, **29**, 1992 (1935).
[233] Hirsch, P., British P. 299,105, July 25, 1927; *Chem. Abs.*, **24**, 3061 (1929).
[234] Redd, W. R., U. S. P. 1,948,239, Feb. 20, 1934, to Millprint Products Corp.; *Chem. Abs.*, **28**, 2923 (1934).
[235] Lehmann, K. B., *Arch. Hyg.*, **106**, 1 (1931); *Chem. Abs.*, **26**, 166 (1932).
[236] Eising, E. H., *Annals of Surgery*, **93**, 1231 (1931); British P. 417,685, Oct. 10, 1934; *Chem. Abs.*, **29**, 1211 (1935). U. S. P. 1,919,055, July 18, 1933; *Chem. Abs.*, **27**, 4879 (1933).
[237] Sheard, C., and Thompson, L., *Proc. Staff Meeting Mayo Clinic*, **6**, 690 (1931); *Chem. Abs.*, **26**, 2764 (1932).
[238] Harris, R. S., Bunker, J., and Milas, N., *J. Bact.*, **23**, 429 (1932); *Ind. Eng. Chem.*, **24**, 1181 (1932).
[239] Sears, H. J., and Black, N., *J. Bact.*, **27**, 453 (1934).
[240] Stevens, F. A., *J. Lab. Clin. Med.*, **21**, 26, 1040 (1935-6); *J. Bact.*, **32**, 47 (1936); *J. Inf. Dis.*, **58**, 185 (1936).

attributed the photoactivity of such products to the evolution of gaseous organic peroxides and aldehydes which diffuse rapidly through a film of cellulose acetate. The plate-fogging and bactericidal effects of the vapor from irradiated cod-liver oil and from ozonide of olive oil were found to be due to substances liberating active oxygen. Not only are bacteria killed by the oxygen liberated from these oils, but their growth rate may be retarded or dissociation may occur if the organisms are subjected to sublethal doses.

Courtesy Westinghouse Electric and Manufacturing Co.

FIGURE 145. Ultraviolet Sterilization of Air in Operating Room.

Reiner-Deutsch and Molnar [241] found irradiation of essential oils in alcohol for fifteen minutes at 25 cm. from a Burdick air-cooled lamp to increase their bactericidal power so that the vapors would kill staphylococci in three hours.

It has been claimed that irradiated metals are bactericidal at a distance [242]

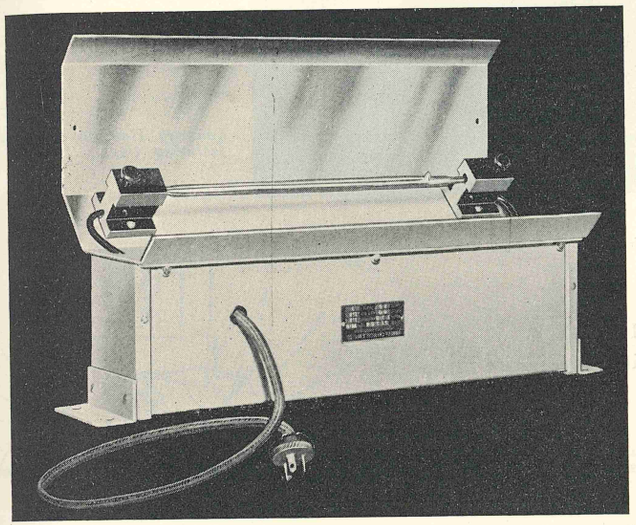
Utilization of Ultraviolet Sterilization in Hospitals.[243] The degree of contamination in an operating room is said to depend on the duration of occupancy, number of occupants in the room, the number of contamination carriers and the degree

[241] Reiner-Deutsch, W., and Molnar, N., *J. Bact.*, **30**, 444 (1935); *Chem. Abs.*, **30**, 1086 (1936).

[242] Ried, O., *Centralbl. Bakt. Parasitenk., Abt. I*, **121**, 267 (1931); Goldberg, I. M., *Acta. Med. Skand.*, **83**, 212, 573 (1934).

[243] Hart, D., *J. Thoracic Surg.*, **6** (1), 4581 (1936). Hart, D., *Surgery*, **1** (5), 770 (1935). Hart, D., *Archives of Surgery*, **34**, 874 (1937). Hart, D., and Gardner, C. E., Jr., *Transactions of the Southern Surgical Associations*, **49**, 377 (1937). Hart, D., *J. Thoracic Surg.*, **7** (5), 525 (1938). Hart, D., *Archives of Surgery*, **37**, 956 (1938). *The Modern Hospital*, **46** (6), June (1936). Hibben, S. G., and Blackburn, P. W., *Electrical Engineering*, 455 (1938).

of contamination in their respiratory passages, the adequacy of masks, the cleanliness of the room and of the incoming air, and the efficacy of the ventilating system. It was found that careful regulation of the above factors to afford maximum protection against entrance of bacteria did not achieve this purpose completely. Members of the operating team constantly breathe bacteria into the air, even though all members wear masks. Presence of bacteria is particularly dangerous in thoracic surgery, where long incisions are made. For this reason, thoracic operations seldom were performed during winter months, when the probability of respiratory contamination in the operating team was highest. The observations of Rentschler and James [244] that air-borne pathogenic bacteria can be killed with about 10 per



Courtesy Hanovia Chemical and Manufacturing Co.

FIGURE 146. Operating Room Safe-T-Aire Equipment for Ceiling or Wall Mounting.

cent of the radiant energy required to kill the same bacteria on a plate led to a method for controlling bacteria in operating rooms. In one type of installation proposed by James and Hart (Figure 145) a bank of eight lamps which emit principally the line 2537A is arranged in a square above the operating table. Rays from these lamps kill bacteria (breathed by members of the operating team) before the bacteria reach the body of the patient. It was stated that the intensity of the ultraviolet rays reaching the operating table is too low to cause harmful aftereffects to the patient. Further, utilization of such lamps was reported to accelerate wound healing.

The effectiveness of bactericidal radiation during extrapleural thoracoplasties has been studied. It was found that mortality was reduced more than 50 per cent by use of radiation during operations, that postoperative infection was avoided almost completely, that postoperative temperature elevations of patients decreased and that wound healing was more rapid. Also, the period required before reopen-

[244] Rentschler, H. C., and James, R. F., in article of Hibben, S. G., and Blackburn, P. W., *Electrical Engineering*, 455 (1938). Rentschler, H. C., Address at Mellon Institute of Industrial Research, March 21, 1939.

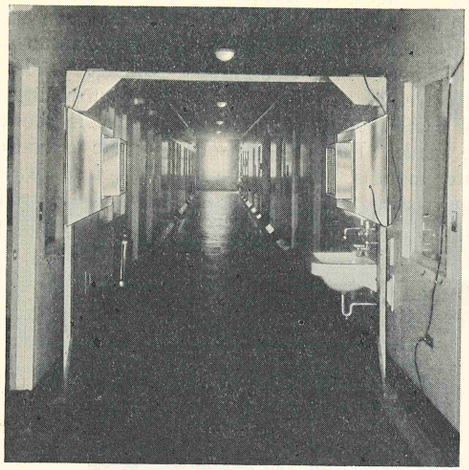


FIGURE 147 (*a*).

Baryaire Safe-T-Aire Equipment.

Courtesy Hanovia Chemical and Manufacturing Co.

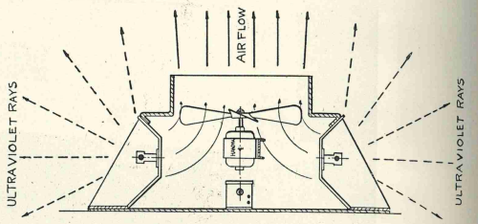


FIGURE 147 (*b*).

Baryaire Safe-T-Aire Equipment.

Courtesy Hanovia Chemical and Manufacturing Co.

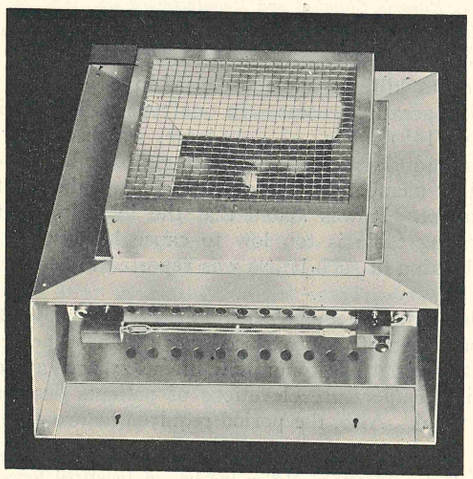


FIGURE 147 (*c*).

Courtesy Hanovia Chemical and Manufacturing Co.

ing of the wound to complete the stages of thoracic surgery was reported to be lessened considerably.

Wells and Brown [245] found it possible by means of the mercury arc to destroy the infectivity for ferrets of the influenza virus (P R 8 strain) suspended in air. Other quartz operating room lamps have been designed (Figure 146) for ceiling or wall mounting. "Baryaire" units (Figure 147) have been devised for use in hospital corridors to prevent cross-infection. It is claimed that microörganisms cannot be carried past the barrier of ultraviolet light.[246]

[245] Wells, W. F., and Brown, H. W., *Am. J. Hyg.*, **24**, 407 (1936); see also Wells, W. F., and Wells, M. W., *J. Am. Med. Assoc.*, **107**, 1698, 1809 (1936).

[246] Note also Magondeaux, B., French P. 729,022, March 9, 1932.

Chapter 36

The Physiological Effects of Ultraviolet Rays

The success attained in the use of ultraviolet light in the treatment of rickets, surgical tuberculosis and certain other conditions discussed in subsequent chapters, stimulated a widespread empirical (and frequently non-critical) use of this treatment for a great variety of diseased conditions. Unwarranted and extravagant claims served to create an undeserved prejudice against even the proper application of this form of therapy. For this reason, before discussing in Chapter 38 the therapeutic applications in which ultraviolet light may serve a useful purpose, it is desirable to consider the present state of our knowledge of the general physiological effects of this form of energy upon multicellular organisms. The preceding chapters have laid the basis for this by enumerating the effects of the rays upon the chemical constituents of cells and upon individual cells as a whole. The way in which generalized irradiation of large areas of the body may produce alterations in the circulation, respiration, the composition of the blood and the growth of the body as a whole or of various of its organs may now be considered.*

In the extensive literature many apparent contradictions abound.

In part, these may be ascribed to inaccurate observations or to too hasty generalizations from an inadequate number of experiments. In part, they are due to a failure to appreciate the necessity of controlling the spectral distribution of the sources employed. Much work calls for repetition under more adequate physical control. In the present survey, it has not been considered possible to undertake a detailed analysis of the adequacy of the experimental approach in the various investigations reported, since for the most part the results are not usually striking. A more critical treatment would demand a much larger amount of space than is justifiable in view of the fact that there are at present available several reviews and books. Only an outline of what appear to be the more significant conclusions is given here.[1]

Comparatively little work has as yet been done on the application of the Einstein law to biological systems, aside from that involved in the photosynthetic mechanism in plants and in the formation of vitamin D_2.[2] There is thus a hiatus between the photochemical theories discussed and applied in Part II of this book and the treatment of the photochemical processes upon which must ultimately depend the physiological responses which occupy a large part of the remainder of this book.

Early workers were inclined to the belief that ultraviolet rays act in some manner by virtue of photoelectric effects, produced when they strike the living organism.[3] This is now recognized to play a role of importance only when the wavelengths employed are far shorter than those available from the sources usually employed under the ordinary conditions of experimental work or practical therapy.[4]

Attention has been drawn by various workers to the possibility that x-rays or radium may owe some of their biological actions to ultraviolet rays produced as a result of the fluorescence of some components of the irradiated systems. As yet this possibility has been relatively little explored.[5]

There have been, among the many suggestions advanced to account for the general reactions underlying the utility of heliotherapy or artificial ultraviolet therapy, a few which have attained special prominence, at least for a time. One group of workers advanced the claim that the effects were due, not to the direct effects of the light rays upon the body surface, but rather to the production in the air of ozone or oxides of nitrogen which when breathed were indirectly responsible for the effects produced. A leading sponsor of this theory was Kestner,[6] who had in mind particularly the use of a carbon arc source. Peemöller[7] asserted that only when the air through which the rays passed was breathed was it possible to observe any effect of the irradiation upon the blood pressure. This theory has been discredited by subsequent workers who have shown that the effects of irradiation on blood pressure cannot be detected if the subject (a dog) is exposed to the irradiated air but protected by filters from the direct action of the rays.[8]

Another view was that physiological alterations may ensue as a result of a stimulation through the eye of the nervous control of the circulation. There is an experimental basis for this in the observation by Reed that in the dog[9] strong irradiation of the retina produces a depression of the blood pressure, usually accompanied by a decrease in the heart rate, which eventually leads to a condition of shock unless the irradiation be discontinued. Nevertheless, there is little reason to believe that under ordinary conditions the reaction of the body to irradiation is brought about by nerve stimulation in the eye and this may be dismissed from further consideration.

Current theories regard the behavior as a response to changes brought about in the skin. Most of the radiations are absorbed in very thin layers of the skin and do not penetrate to the lower tissues. One process which occurs in the skin, the conversion of certain sterols into the vitamins of the D group is definitely known to account for the beneficial results of irradiation in the prevention and treatment of rickets, and there is an accumulating body of evidence that this may also account, in part at least, for the beneficial results in tuberculosis. There are, however, undoubtedly other processes induced in the skin which are less well understood. The visible changes in sunburn have been attributed to the production of histamine-like materials which then act upon the vessel walls and produce the local erythema. Such substances may enter the blood stream and be carried to the nervous tissues which control the fundamental physiological processes. Such substances may also conceivably exert a control through a local stimulation of certain afferent nerves. Viale and Roncallo[10] find that although irradiation of a normal

* The conversion of sterols into vitamin D and its application is deferred to Chapters 38, 39 and 40.

[1] Laurens, H., "The Physiological Effects of Radiant Energy," American Chemical Society Monograph Series, New York, Reinhold Publishing Corp., 1933; "The Biological Effects of Radiation." Edited by Duggar, B. M., 2 Vols., New York, McGraw-Hill Book Company, Inc., 1936.
Review articles: Valentin, H., *Pharm. Ztg.*, **75**, 982, 995, 1005 (1930); *Chem. Abs.*, **25**, 120 (1931); Levine, V. E., *Arch. Phys. Therapy, X-Rays & Radium*, **12**, 197, 267, 389 (1931); Packard, C., *Quart. Review Biol.*, **6**, 253 (1931); Snyder, C. D., *Ibid.*, 281; Frankenburger, W., *Strahlentherapie*, **27**, 233 (1933); de Toni, G., *Biochim. terap. sper.*, **22**, 547, 577 (1935); **23**, 75 (1936).

[2] Warburg, O., *Trans. Faraday Soc.*, **27**, 551 (1931).

[3] Clark, J., *Physiol. Rev.*, **2**, 277 (1922).

[4] See, however, Saidman, J., *Compt. rend.*, **180**, 693 (1925); Gallerani, G., *Boll. soc. ital. biol. sper.*, **11**, 817 (1936); *Chem. Abs.*, **31**, 7759 (1937).

[5] See Spiegel-Adolf, M., *Klin. Wochschr.*, **9**, 1615 (1930).

[6] Kestner, O., *Z. Biol.*, **73**, 1, 7 (1921); **77**, 245 (1922).

[7] Peemöller, F., *Klin. Wochschr.*, **2**, 973 (1923); note also Secchi, C., *Pediatria Rivista*, **35**, 1111 (1927); *Chem. Abs.*, **22**, 1786 (1928).

[8] Laurens, H., and Mayerson, H. S., *Am. J. Physiol.*, **84**, 524 (1928).

[9] Reed, C. I., *Am. J. Physiol.*, **65**, 477 (1923).

[10] Viale, G., and Roncallo, E., *Boll. soc. ital. biol. sper.*, **10**, 311 (1935); *Chem. Abs.*, **30**, 6014 (1936).

rabbit's foot depresses the blood sugar, this effect is not found if the nerves to the foot are first cut. Furthermore, section of the right vagus nerve at the neck also interferes with the fall in blood sugar which usually follows irradiation.[11]

Other views assume that light absorbed by the blood in dilated skin capillaries alters its constitution. Others view the circulatory effects as due primarily to the shift of blood into dilated skin capillaries, that is to a localized hyperemia. This view is particularly advanced in explaining the results of the longer wave-lengths used in heliotherapy. Sonne[12] made determinations of skin and subcutaneous temperatures during irradiation, as a result of which he concluded that the visible and shorter infrared rays produce local temperatures greater than those observed in fevers. His work is of importance in affording some measure of explanation of the differences in the effects produced by sunlight and carbon arc light from those due to the mercury arc which produces less of these rays and more of the short ultraviolet rays.

Another group of German workers regard the effects of general irradiation as due to a generalized protein shock similar to that after the injection of milk or other non-specific proteins. The shock is assumed to result from the introduction into the circulation of the products produced by the destruction of proteins in the cells of the skin. This is particularly adapted to the explanation of the effects following mercury-arc irradiation.

Rothmann[13] believed the general response due to a lowering of the tone of the sympathetic system.

Effects on the Skin[14]

During exposure of the skin to sunlight, an immediate reddening is usually observed. This is a heat erythema due to the longer visible and infrared rays. It is not strictly localized in the irradiated parts and disappears shortly after the irradiation is stopped.

The erythema due to the ultraviolet rays of sunlight is produced only after a latent period of from one to ten hours. It is seen only in the irradiated areas and varies in severity with the intensity and duration of the exposure, blistering accompanying the more intense or longer doses. The erythema persists for several days and is then replaced by an area of pigmentation, the upper epidermal layers scaling off. The pigmentation may persist for several months. These effects were first described in detail by Finsen who employed a carbon arc as the source of light.

During the erythema there is a widening of the capillary blood vessels and at its height, there is leucocytic infiltration and degeneration, particularly of the cells of the Malpighian layer. These later dry to a scale above a regenerated pigmented skin.[15]

Ultraviolet radiations are highly absorbed by the skin. Exact measurements of their penetrability are difficult because a portion of the shorter wave-lengths are converted by fluorescence into longer ones in the blue and other portions of the visible region and these have greater penetrability. Vlès and Ugo[16] find the

[11] Martini, E., and Roncallo, E., *Boll. soc. ital. biol. sper.*, **11**, 77 (1936); *Chem. Abs.*, **30**, 6063 (1936).

[12] Sonne, C., *Acta Med. Skand.*, **54**, 336 (1921); **56**, 619 (1922); *Acta Radiologica Skand.*, **5**, 419 (1926); *Chem. Abs.*, **21**, 1139 (1927).

[13] Rothmann, H., *Klin. Wochschr.*, **2**, 881 (1923); Petersen, W. F., and v. Oettingen, W. F., *Arch. Exptl. Path. Pharmakol.*, **123**, 160 (1927).

[14] *Cf.* Waller, M. D., *Proc. Roy. Soc.*, **108B**, 259 (1931), and for a general discussion, Eidinow, A., *Brit. J. Tuberculosis*, **22**, 136 (1928).

[15] For histological details, see Keller, P., *Strahlentherapie*, **16**, 52 (1924); **28**, 152 (1928); Uhlmann, E., *Ibid.*, **40**, 765 (1931). See also Rost, G. A., and Keller, P., in Jadassohn, "Handbuch der Haut und Geschlechtskrankheiten," Vol. **2**, Berlin, J. Springer, 1929.

[16] Vlès, F., and Ugo, A., *Compt. rend. soc. biol.*, **123**, 226 (1936); *Chem. Abs.*, **31**, 713 (1937).

fluorescence spectrum of shaved rat skin to be in part that of the proteins and in part that of cholesterol. Pauli[17] states that the fluorescence curve is to a large extent coincident with the erythema curve. Rabbit skin shows a fluorescence between 5400 and 4200 with a maximum at 5000A. That of human skin has its maximum at 4600A.

Hasselbalch[18] gave the results indicated in Table 24 for the penetration of the rays from a Kromayer water-cooled quartz mercury lamp. Anderson and Macht,[19]

Table 24.—Penetration of Rays from Kromayer Lamp.

	Wave Length in Millimicrons							
	436	405	366	354	313	302	297	289
Per cent transmitted by skin 0.1 mm. thick	59	55	49	42	30	8	2	0.01
By skin 1.0 mm. thick	0.5	0.3	0.08	0.02	0.006			

who agreed that dead skin is practically opaque to wave-lengths shorter than 3660A, claimed that live rabbit skin has a much greater transparency, transmitting from 6 to 10 per cent of the energy at wave-lengths between 2537 and 3000A. Bachem and Reed,[20] however, were able to find but little difference between live

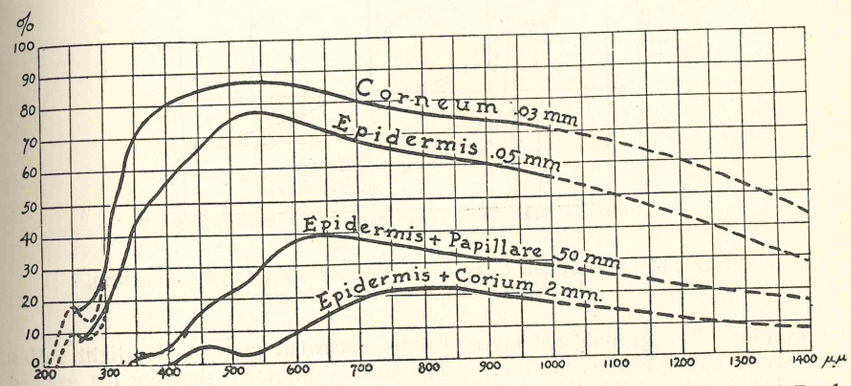


Figure 148. Transmission Curves for the Various Skin Layers (Bachem and Reed, *American Journal of Physiology*).

and dead skin if the specimen was kept moist and tightly stretched. They found the wave-lengths of the near infrared and visible regions strongly absorbed by the blood of the corium and subcutaneous layers. The far infrared rays have very little penetrating power and are absorbed in the epidermis. Some of their data are reproduced in Figure 148. The absorption of a band with maximum at 2800A is very great in the corneum and prickle cell layers. On both sides of this band near 3000 and 2500A, the penetration is greater, more radiation reaching the Malpighian layers and the corium.

[17] Pauli, W. E., *Strahlentherapie*, **26**, 577 (1927); *Chem. Abs.*, **22**, 3672 (1928).

[18] Hasselbalch, K. A., *Skand. Arch. Physiol.*, **25**, 55 (1911); *Chem. Abs.*, **5**, 2862 (1911).

[19] Anderson, W. T., Jr., and Macht, D. I., *Am. J. Physiol.*, **86**, 320 (1928).

[20] Bachem, A., and Reed, C. I., *Am. J. Physiol.*, **97**, 86 (1931); **90**, 600 (1929).

Bachem [21] has also given data on the ultraviolet transparency of the various layers of the human skin. Figure 149 indicates that the horny layer is very transparent in the visible and near ultraviolet. At 3000A a strong absorption band begins, which has its maximum at 2800A and then diminishes to a minimum at 2600A, increasing again at shorter wave-lengths, and recalling the absorption of

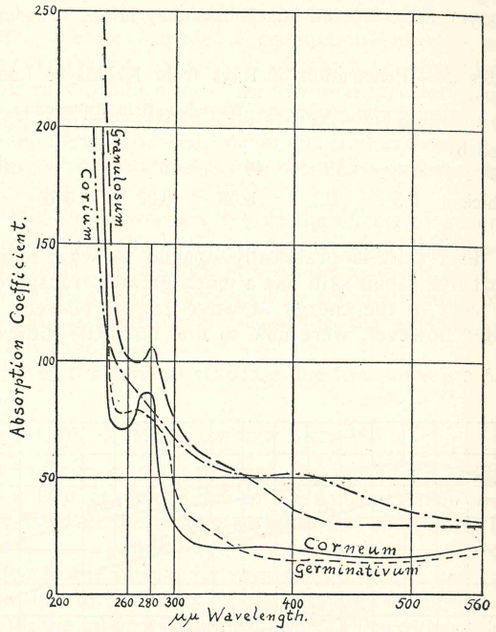


FIGURE 149. Absorption Curves for Various Skin Layers (Bachem, *American Journal of Physiology*).

the proteins. The granulosum layer absorbs somewhat more visible light. Most transparent is the germinating layer. The corium differs in showing the greatest absorption for the visible light. It also shows no absorption maximum at 2800A and has somewhat lower absorption coefficients in the more extreme ultraviolet range. Bachem believes the erythema to originate in the stratum germinativum or corium under the shadow of the upper layers.

Lucas [22] has discussed particularly the difficulties involved in this type of measurement. He expressed his results merely in terms of the relation between the logarithms of incident and transmitted light. His observations indicated the skin used to be a hundred to ten thousand times more opaque than that studied by Hasselbalch, much of the loss of radiant energy being due to scattering. In the living animal, however, much of the scattered light may not be lost to the animal. Lucas was unable to detect the passage of any line shorter than 3130A through 0.2 mm. of skin in exposures less than 24 hours. With very thin specimens of epidermis obtained from blisters of the forearm, Lucas obtained the results

[21] Bachem, A., *Am. J. Physiol.*, **91**, 58 (1929).
[22] Lucas, N. S., *Biochem. J.*, **25**, 57 (1931).

of Figure 150, which appear to resemble greatly the curves for the absorption of the amino- acids, tryptophane and tyrosine. These observations appear chiefly of value in demonstrating the extreme difficulty of the problem of measuring the absorption of the skin as a whole, since they had to be limited largely to the epidermis. They do, however, demonstrate that the penetration of ultraviolet rays cannot be more than very slight. Pauli [23] claims that glycerol containing a little alcohol is the best agent for increasing the ultraviolet permeability of the skin.

By the use of a monochromator, Hausser and Vahle [24] determined the relative degrees of erythema produced by the various mercury-arc lines, each being adjusted

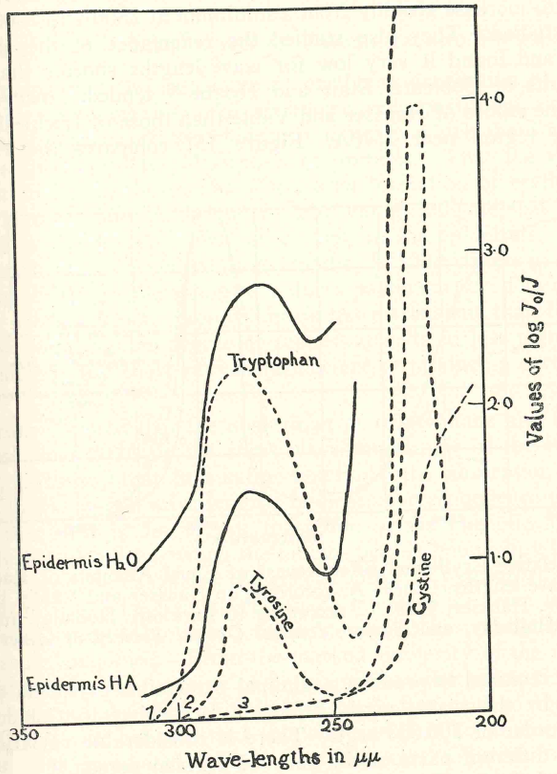


FIGURE 150. Absorption of Skin from a Blister (From Lucas, *Biochemical Journal*).

to the same intensity. They found a maximum sensitivity at 2970A, the effect beginning at 3130A. Wave-lengths in the visible and longer ultraviolet had no effect. Adopting the intensity of the erythema produced by the 2970A line as 100 per cent, the relative values found on irradiation by the other wave-lengths were found to be as indicated in Table 25. In later work, they found a second maximum

[23] Pauli, W. E., *Strahlentherapie*, **26**, 577 (1927); *Chem. Abs.*, **22**, 3672 (1928).
[24] Hausser, K. W., and Vahle, W., *Strahlentherapie*, **13**, 41 (1921); **27**, 348 (1928); Henri, V., and Moycho, V., [*Compt. rend.*, **158**, 1509 (1914)] early placed the maximum irritating effect on rabbit's ear at 2800A.

Table 25.—Effect of Wave-Length on Erythema.

Wave-Length (A)	Erythema (%)
Greater than 3130	None
3130	4.5
3020	58.
2970	100.
2890	30
2800	28

at 2500A. Luckiesh, Holladay and Taylor,[25] using a filter method, confirmed the existence of the maximum at 2970A but found at the shorter wave-lengths values which tended to increase steadily from a minimum at 2800A to 2400A, the shortest wave-length studied. They also studied the reflectance of the skin for various wave-lengths and found it very low for wave-lengths shorter than 3100A. The erythema results of Coblentz, Stair and Hogue[26] tended, however, to resemble more closely the values of Hausser and Vahle than those of Luckiesh, Holladay and Taylor at the region near 2540A. Figure 151 compares the results of these workers.

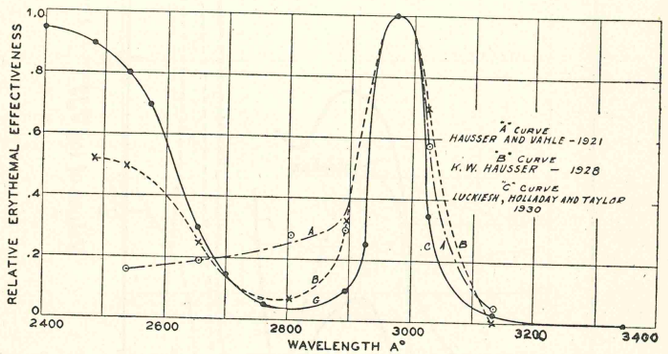


FIGURE 151. Relative Erythemal Effectiveness of Equal Amounts of Radiant Energy at Various Wave-lengths. Curve A, according to Hausser and Vahle, 1921; B, according to K. W. Hausser, 1928; C, according to Luckiesh, Holladay and Taylor, 1930. (Luckiesh, Holladay, and Taylor, *Journal Optical Society of America*).

The energy required to produce a minimal perceptible erythema on a sq. cm. of untanned skin by the wave-length 2970A is, according to Coblentz, Stair and Hogue, of the order of 500,000 ergs. There is considerable variation in different persons and in different parts of the body of a given person.[27]

Luckiesh and Taylor[27a] find that to produce tanning, exposures to artificial or natural sunlight sufficient to give an appreciable erythema are required. Repeated suberythemal doses usually do not tan, although they may be effective in the cure of rickets. With an S-4 sunlamp emitting chiefly narrow bands at 2967, 3022 and 3130A, an exposure of four minutes at a distance of 2.5 feet was

[25] Luckiesh, M., Holladay, L. L., and Taylor, A. H., *J. Opt. Soc. Am.*, 20, 423 (1930).

[26] Coblentz, W. W., Stair, R., and Hogue, J. M., *Bureau Standards J. Research*, 7, 723 (1931); 8, 541, 759 (1932).

[27] See also Adams, E. Q., Barnes, B. T., and Forsythe, W. E., *J. Opt. Soc. Am.*, 21, 207 (1931); Uhlmann, E., *Strahlentherapie*, 35, 361 (1930); Hausser, K. W., and Schlechter, E., *Ibid.*, 27, 348 (1928); Keller, P., *Ibid.*, 34, 129 (1929); 35, 353 (1929).

[27a] M. Luckiesh and A. H. Taylor, *J. Am. Med. Assoc.*. 112. 2510 (1939).

found necessary to produce on the human arm a minimal perceptible erythema visible one day after the irradiation. To produce a minimal perceptible tanning visible two months later, an exposure of 7.5 minutes was required. These authors also give a curve showing the relative tanning effectiveness of various wave-lengths. It is in general similar to the erythema curve except at the regions on either side of the maximum. Wave-lengths of 2500-2600A are ineffective in tanning, although they may cause a strong erythema. There is some evidence that wave-lengths longer than 3300A may produce immediately after exposure a brownish pigmentation with but little inflammation. This is of little practical significance since the energy densities and times of exposure required are prohibitive.

Mechanism of the Production of Erythema and Pigmentation

It must be noted that the maximum of erythema production at 2970A corresponds to the absorption maximum of no known cell constituent, notwithstanding the observations of Lucas upon the epidermis alone, in which there was observed a fair degree of similarity to the absorption of proteins. That the wave-length of greatest absorption lies in the region of the least formation of erythema has been interpreted by Hausser and Vahle and by Bachem to indicate that erythema is a process effected in the deeper layers rather than in the epidermis. There is evidence that the erythema produced by wave-lengths of 2500A differs in character from that produced at 2970A in the shade of redness particularly. The reaction to the shorter rays is produced more rapidly and is more transient than that due to the longer ones and, for the same degree of redness, results in less pigmentation, provided the exposure to the short rays is insufficient to produce a severe and lasting burn.

Frankenburger[28] noted that the absorption of tryptophane and tyrosine occurs at wave-lengths about 200A on the short wave-length side of the erythema curve. He points out, however, that in alkaline solutions, the absorption of tyrosine at least is shifted to the longer wave-lengths in closer correspondence to the erythema curve. Since this shift is due to salt formation of the phenolic hydroxyl group, it could conceivably also occur when the amino- acid is bound in a protein. For a given incident energy, he calculated the energy effectively absorbed by the tyrosine contained in 80 micra of epidermis beneath 25 micra of corneum and compared it with that of alkaline tyrosine solutions in concentrations roughly equivalent to those in the tissues examined. From the marked similarity of the resulting curves he concluded absorption by tyrosine to be essential to the production of erythema. Although the tyrosine absorbed only from 4 to 13 per cent of the total incident energy at 2970A, it was believed that this was sufficient to produce the erythema. Frankenburger also irradiated 0.4-per cent aqueous solutions of *l*-tyrosine in quartz tubes with unfiltered light from a mercury arc. In air-free water no chemical or spectrographic changes could be detected within six hours. But in the presence of air, the tyrosine quickly changed through a yellow to a deep brown color and carbon dioxide was evolved. Frankenburger believed, as many have, that tyrosine forms first oxindo- compounds and then melanins which are components of the pigment of the skin. During irradiation the absorption increased and extended into the visible region in agreement with the spectra of melanins. Spiegel-Adolf obtains photosynthetic melanins by irradiating tyrosine or tryptophane in alkaline solution or phenylalanine in neutral solution.[29]

[28] Frankenburger, W., *Naturwiss.*, 21, 116 (1933).

[29] Spiegel-Adolf, M., *Biochem. J.*, 31, 1303 (1937).

That the process underlying erythema formation is not that of a simple protein coagulation was the conclusion of Clark[30] from a comparison of the temperature coefficients of the two types of reaction. That for erythema formation is 2.3 in human and 1.9 in frog skin, but that of the coagulation of proteins (at least in its second stage) is very high, being over ten.

The production of melanin by irradiation of the skin has been effected by Lignac,[31] but irradiation of four minutes produced the same amount of pigmentation in live skin as several hours of irradiation in dead skin.[32] Schmalfuss, Bussmann and Nickelsen[33] believe skin contains other dye-forming substances than tyrosine, capable of darkening without enzymes in light. Intense solar irradiation of a normally pigmented individual causes the appearance of a melanin reaction, the Thormaehlen reaction, in the urine, but this is not observed in the case of previously irradiated and tanned individuals.[34]

The administration of vitamin C does not affect the pigmentation of human beings following ultraviolet irradiation, according to von Drigalski.[35] On the other hand, Schade[36] believed the daily administration of this vitamin for ten days after irradiation with an Alpine lamp prevented subsequent pigmentation. Balakhovskii[37] claimed the application of carotene in water or dilute alcohol to be beneficial in curing ultraviolet burns.

Lewis has long considered histamine or histamine-like substances of importance in the production of erythema, whether by irradiation or by heat, mechanical or electrical causes.[38] The mechanism of their liberation by irradiation does not appear to be a nervous one, since erythema may be produced after the nerves supplying the skin have been cut. Novocaine injected intradermally does lessen erythema formation, but this may be due to an internal filtering action. Krogh[39] believes that, although histamine may be formed, the predominant dilating compound in ultraviolet erythema must be a material of extremely low diffusibility. Otherwise it would diffuse into the blood through the enormous surface of the dilated blood vessels and thus be lost.

In a preceding chapter, mention was made of the belief of Ellinger that histamine may be photochemically produced by the decarboxylation of histidine. Frankenburger, however, pointed out that the absorption of histidine is great only at wave-lengths too short to permit the erythema curve to be accounted for by a direct action on histidine. He did, however, suggest that when this amino- acid is bound in peptide linkages, its absorption spectrum might be sufficiently displaced toward the longer wave-lengths to permit some absorption and photochemical change. He also described the production of a new absorption band at 3150 to 3200A during the irradiation of histidine solutions in the absence of oxygen. This new absorption did not resemble that of histamine, and histamine itself when irradiated also exhibited a new type of longer wave-length absorption. From his

[30] Clark, J., *Am. J. Hyg.*, **24**, 334 (1936).

[31] Lignac, G., *Nederland. Maanschr. Geneesk.*, **16**, 496 (1930); *Chem. Abs.*, **24**, 1873 (1930).

[32] See also Lovisatti, N., [*Forsch. Geb. Röntgenstrahlen*, **44**, 235 (1931); *Chem. Abs.*, **25**, 5679 (1931)] for the function of the melanotic pigments in increasing the ultraviolet tolerance.

[33] Schmalfuss, H., Bussmann, G., and Nickelsen, O., *Arch. Dermatol. Syphil.*, **175**, 39 (1937); *Chem. Abs.*, **31**, 5422 (1937).

[34] Risak, E., and Asperger, H., *Klin. Wochschr.*, **11**, 154 (1932); *Chem. Abs.*, **26**, 3553 (1932).

[35] von Drigalski, W., *Klin. Wochschr.*, **13**, 1374 (1934); *Chem. Abs.*, **29**, 1138 (1935); Tenchio, F., *Klin. Woch.*, **13**, 1511 (1934); *Chem. Abs.*, **29**, 1139 (1935).

[36] Schade, H., *Klin. Woch.*, **14**, 60 (1935); *Chem. Abs.*, **29**, 4045 (1935).

[37] Balakhovskii, S., *Compt. rend. acad. sci. U.R.S.S.*, **1**, 28 (1934); *Chem. Abs.*, **28**, 2736 (1934).

[38] Lewis, T., "The Blood Vessels of the Human Skin and Their Responses," London, Shaw and Sons, 1927.

[39] Krogh, A., "The Anatomy and Physiology of the Capillaries," New Haven, Yale University Press, 1929.

observations it would appear that in irradiated histidine solutions, histamine could at best be present in very slight concentrations, probably insufficient to account for the vasodilatation of erythema. Ellinger[40] found no difference in effects on the blood pressure of the cat or on the surviving guinea pig intestine of extracts prepared from skin before and after ultraviolet irradiation. Frankenburger concludes that the erythema reaction is a complex one, since strong erythema can be produced in the range of wave-lengths (3100 to 2750A) which fail to affect histidine. Accordingly, if histamine or some other erythema-producing substance is formed it must be indirectly produced. He also suggested that the changes induced in tyrosine are accompanied by changes in the protein of which it forms a part and that these are of a nature which increases the permeability of the membranes releasing substances of histamine-like nature normally present in cells.

Various workers have attempted to correlate the temperature of the skin when irradiated with the severity of the effects produced. Thus, Shattock and Waller[41] believe that if the tissues are heated simultaneously with or shortly after exposure, the erythema is delayed or suppressed. On the other hand, exposure to heat before the irradiation increases the erythema produced. Hill[42] and Eidinow also believed that hyperemia tends to increase the effects of irradiations with the quartz lamp. Schall and Alius,[43] and Cramer and Fechner,[44] however, found little if any such effect.

Lehner and Urban[45] observed that repeated exposure of a definite area of normal skin produced after the first few treatments a more prompt and intense reaction, but after about three treatments there was little itching and scarcely any hyperemia. At the same time the spot so treated became less sensitive to other irritants, such as the injection of morphine. Ten minutes after the exposure of the entire back to the lamp, the skin of the breast or upper arm was more sensitive than normally to the injection intracutaneously of morphine solutions, but this hypersensitivity persisted for only thirty minutes. It has been stated that by giving repeated doses the skin may be induced to develop a tolerance to ultraviolet light so that the sensitivity may be reduced to as low as 8 per cent of its normal value for the individual. The filtering action of the pigments produced may play some part in this acquired tolerance, but other factors are probably concerned. Relatively little is known exactly about the production of tolerance. Antibodies do not seem to be concerned.

Sensitization of the skin has been observed. After rats have been injected intraperitoneally with chlorophyll, the erythema and hyperemia produced on irradiation of a portion of the skin were much more pronounced than in uninjected animals, according to Fulchignoni.[46] There has also been reported a case in which an alcoholic solution of chlorophyll when rubbed on the skin penetrated to the deeper layers and sensitized it so that a short exposure of the treated part to red or to ultraviolet light produced erythema, although the surrounding untreated parts were unaffected.[47] Proft[48] found some soaps to increase the erythema due to light. This he believed to be independent of the presence of a sensitizing dye such as chlorophyll or the pigment of linseed oil, and also independent of the horny epithelium. Instead, he believed it due to the presence of free alkali. A weakened erythma results from the use of oils, fats and undissolved soaps and absolute protection was afforded by a 10-per cent alcoholic salicylic acid solution. The pH of the skin alters its light sensitivity, according to Marchionini and Hövelborn,[49] who found that pretreatment with a salve of pH 2.7 increased its sensitivity. Skin treated with an alkaline salve required two and a half

[40] Ellinger, F., *Arch. Exp. Path. Pharmakol.*, **149**, 343 (1930).

[41] Shattock, F., and Waller, M. D., *Lancet*, **II**, 917 (1929).

[42] Hill, L., and Eidinow, A., *Lancet*, **II**, 299 (1924); see also Török, L., Lehner, E., and Urbán, F., *Krankheitsforsch.*, **5**, 293 (1927); *Chem. Abs.*, **22**, 4167 (1928).

[43] Schall, L., and Alius, H. J., *Strahlentherapie*, **26**, 649 (1927); **27**, 769 (1927-8).

[44] Cramer, H., and Fechner, G., *Ibid.*, **39**, 474 (1931).

[45] Lehner, E., and Urbán, F., *Krankheitsforsch.*, **4**, 381 (1927); *Chem. Abs.*, **22**, 4166 (1928).

[46] Fulchignoni, E., *Boll. soc. ital. biol. sper.*, **11**, 428 (1936); *Chem. Abs.*, **31**, 1053 (1937).

[47] Kitchevatz, M., *Compt. rend. soc. biol.*, **116**, 675 (1934); *Chem. Abs.*, **28**, 5839 (1934); *Ann. de Dermat. et Syph.*, **5**, 293 (1934).

[48] Proft, H., *Strahlentherapie*, **40**, 351 (1931); *Chem. Abs.*, **25**, 3675 (1931).

[49] Marchionini, A., and Hövelborn, C., *Arch. Dermatol. Syphilis*, **174**, 251 (1936); *Chem. Abs.*, **30**, 7591 (1936).

times as much exposure as the acid-treated skin to produce an erythema. Papcke[50] believes peroral administration of an isotonic mixture of calcium, potassium and magnesium salts to decrease the erythemic response.

Irradiation of the skin of the guinea pig previously injected with methylene blue decolorizes it irreversibly. The skin of the frog similarly colored is decolorized in darkness but the color is restored on irradiation.[51] Wohlgemuth and Sugihara[52] found suitable irradiation of a guinea pig with natural or artificial sunlight to cause in the skin an increase of the enzyme phenolase, some decrease in lipase and a notable decrease in diastase. The blood enzymes were not affected. Other workers have shown therapeutic doses of ultraviolet light to affect the intracellular oxidase, peroxidase and catalase of the skin. Natural sunlight injures somewhat the ability of the skin to produce lactic acid, but artificial sunlight is more injurious and x-rays even more so.[53] Harpuder[54] found irradiation of the skin up to beginning erythema to affect the diffusion of chloride, calcium and potassium ions. Changes in the contents of water, sodium, potassium and calcium in the pigmented skin of rabbits after its irradiation by ultraviolet rays proceed in the same direction and reach the same values as in unpigmented skin.[55] The contents of sugar and glycogen in pigmented skin are less than in unpigmented skin, but the changes on irradiation proceed alike. No habituation could be observed in the changes in mineral and carbohydrate metabolism of the skin after irradiation.

Skin irradiated with ultraviolet light shows an increase in cholesterol content of from 7 to 150 per cent, according to Roffo.[56] The skin from various parts of the face contains from two to seven times as much cholesterol as skin from the abdomens of the same persons, and the distribution in the face is roughly proportional to the amount of exposure to the sun. Roffo also believed that there was a direct relationship between the frequency of skin tumors and the proportion of cholesterol in the skin. If white rats are kept in darkness there is a lowering of the cholesterol content of the skin.[57] These results were confirmed by Kawaguchi.[58]

Loewy and Cronheim[59] find that the non-protein nitrogen of rat or guinea-pig skin is not affected by five hours of irradiation. The chlorine content decreased either in darkness or under ultraviolet irradiation. Potassium was lowered by irradiation and unaffected by darkness in the rat but increased in guinea-pig skin. Magnesium was increased by irradiation but the calcium content was not altered. Beck[60] claimed local applications of a Vitrisol preparation made by prolonged irradiation of spinach gave good results in the treatment of acne vulgaris and lupus vulgaris. In the repair of cutaneous lesions, cholesterol has the greatest healing action, followed by irradiated ergosterol and then ergosterol.[61] It has been stated that in scleroderma, treatment with massive doses of the vitamin reduces the abnormal calcium deposits from the skin before that element is removed from the bones.[62] The antigen-antibody reaction in skin is inhibited by ultraviolet irradiation, according to Albus and Feldermann.[63] The total

[50] Papcke, G., *Arch. Dermatol. Syphilis,* **168,** 476 (1933); *Chem. Abs.,* **28,** 525 (1934).

[51] Dubouloz, P., and Rochette, J., *Compt. rend. soc. biol.,* **122,** 221 (1936); *Chem. Abs.,* **31,** 3069 (1937).

[52] Wohlgemuth, J., and Sugihara, N., *Biochem. Z.,* **163,** 260 (1925).

[53] Wohlgemuth, J., and Ikebaka, T., *Biochem. Z.,* **186,** 43 (1927); *Chem. Abs.,* **21,** 3632 (1927).

[54] Harpuder, K., *Z. ges. Exptl. Med.,* **76,** 724 (1931); *Chem. Abs.,* **26,** 4834 (1932).

[55] Kaplanskiĭ, S. Y., and Kaplanskaya-Raiskaiya, S. I., *Arch. sci. biol. (U.S.S.R.),* **39,** 169, 175 (1935); *Chem. Abs.,* **30,** 7185 (1936).

[56] Roffo, A. E., *Bol. inst. med. exptl. estudio cancer, No. 39,* 358, 390 (1935); Roffo, A. H., Jr., *Ibid.,* **41,** 41 (1936); *Chem. Abs.,* **31,** 4347 (1937); *Bol. ist. Med. Exptl.,* **6,** 370 (1929); *Chem. Abs.,* **26,** 1304 (1932); *Compt. rend.,* **201,** 566 (1935).

[57] Roffo, A. H., *J. Physiol. Path. Gén.,* **29,** 739 (1931); *Chem. Abs.,* **26,** 2993 (1932); *J. physiol. Path. Gén.,* **30,** 345 (1932); *Chem. Abs.,* **26,** 5330 (1932); *Bol. inst. med. exptl.,* **8,** 32 (1931); *Chem. Abs.,* **29,** 5871 (1935); *Arch. elect. med.,* **42,** 425 (1934); *Chem. Abs.,* **31,** 6682 (1937); Roffo, A. E., Jr., *Bol. inst. med. exptl. estudio cancer,* **14,** 447 (1937); *Chem. Abs.,* **32,** 3812 (1938).

[58] Kawaguchi, S., *J. Biochem. Japan,* **15,** 111 (1932); *Chem. Abs.,* **26,** 2995 (1932); see also Chorozak, T., *J. Physiol. Path. Gén.,* **31,** 408 (1933); *Chem. Abs.,* **28,** 3473 (1934).

[59] Loewy, A., and Cronheim, G., *Biochem. Z.,* **256,** 411 (1932).

[60] Beck, H., *Münch, med. Woschr.,* **74,** 1129; *Chem. Abs.,* **22,** 4655 (1928). For the use of Viosterol in acne, see Doktorsky, A., and Platt, S. S., *J. Am. Med. Assoc.,* **101,** 275 (1933).

[61] Tautini, E., *Sperimentale,* **89,** 712 (1935); *Chem. Abs.,* **30,** 7696 (1936); see Kemmler, H., *Mitt. Grenzg. Med. Chir.,* **43,** 453 (1934); *Chem. Abs.,* **29,** 5927 (1935).

[62] Cornbleet, T., and Struck, H. C., *Arch. Dermatol. Syphilol.,* **35,** 188 (1937); *Chem. Abs.,* **31,** 1487 (1937).

[63] Albus, G., and Feldermann, F., *Klin. Wochschr.,* **17,** 1702 (1938); *Chem. Abs.,* **32,** 6677 (1938).

glutathione of rabbit skin appears to be increased following irradiation, probably because of a disintegration of tissue proteins.[64]

Sunburn Creams and Protective Salves. A great number of skin creams for the prevention of sunburn are on the market and some contain materials which simulate a tan.[65] Malowan[66] states that the ointments which protect fluoresce strongly in ultraviolet light. Prominent constituents are naphtholsulfonic acid, and esculin and its homologs. Eder and Freund[67] propose salves or emulsions containing in addition to esculin or naphtholsulfonic acid, lithopone or a compound of titanium. Dunning[68] suggested the use of the sodium salt of a mono- or di-sulfonic acid of *o*- or *p*-hydroxybiphenyl. Hall[69] employs a polyhydric alcoholic ester of salicylic acid, such as glycerol or glycol mono-salicylate with a mineral oil, or with stearic acid, lanolin, beeswax, etc. Stockelbach[70] employs menthyl salicylate in a vehicle of alcohol, an oil or a cosmetic cream for preventing sunburn. Risler[71] mixed a phosphorescent zinc sulfide with about six times as much of a cream phase made by heating and mixing together stearic acid 170, glycerol 210, water 569, and 10-per cent aqueous ammonia, 50. When cold, one part of violet essence was added.

The I. G. Farbenindustrie[72] proposed such substances as aryl benzimidazoles or aryl benzothiazoles. Issermann, Ohlsson and Orelup propose about 0.5 to 1 per cent of an amino- or substituted amino-benzoic acid, as benzylamino-*o*-benzoic acid, in peanut or almond and mineral oils.[73] Jordan suggests dibenzalacetone as an effective component.[74]

In the past, quinine bisulfate was frequently employed in salves to act as an internal filter.[75] Other materials specified in the I. G. Farbenindustrie patents included stilbene, 2-phenylindole, α-phenylcinnamonitrile, 2-phenylquinoline, N-acetylcarbazole, μ-methylnaphthoxazole and 2-acetyl-3-bromoindazole. Schwarz suggests a cream containing oak bark extract.[76] Sodium phenylbenzimidazolesulfonate or other substances with sharp absorption of wave-lengths in the range 3200 to 3500A are claimed by Merkel and Wiegand to absorb noxious rays without excluding tanning rays.[77]

It has been claimed that sunburn does not follow exposure after vitamin C has been given intravenously and bergamot oil has been applied to the skin.[78]

[64] Matusis, I. I., and Grechanovskiĭ, *Bull. biol. med. exptl. U.R.S.S.,* **3,** 489 (1937); *Chem. Abs.,* **32,** 8449 (1938).

[65] For general discussions see: Lendle, A., *Pharm. Ztg.,* **81,** 903 (1936); Stambovsky, L., *Drug and Cosmetic Ind.,* **36,** 551, 554 (1935); Van Itallie, P. H., *Drug Trade News,* **12,** No. 8, 41, 44, 45, 47 (1937); Augustine, J., *Riechstoff Ind. Kosmetik,* **11,** 218 (1936); Karl, P., *Ibid.,* **12,** 92 (1937); Goodman, H., *Am. Perfumer,* **34,** No. 6, 47 (1937); Böhme, H., and Reichert, B., *Arch. Pharm.,* **275,** 437 (1937); Kalisch, J., *Drug Cosmetic Ind.,* **42,** 52 (1938); Heber, C. F., *Svensk Kem. Tids.,* **50,** 144 (1938); Calame, A., *Seifensieder-Ztg.,* **65,** 456 (1938); Gattefossé, *Parfumerie moderne,* **32,** 97, 113 (1938).

[66] Malowan, L. S., *Seifensieder-Ztg.,* **61,** 335, 353 (1934); *Chem. Abs.,* **28,** 4836 (1934).

[67] Eder, J. M., and Freund, L., Austrian P. 138,527, Aug. 10, 1934; *Chem. Abs.,* **29,** 558 (1935).

[68] Dunning, F., U. S. P. 2,015,005, Sept. 17, 1935; *Chem. Abs.,* **29,** 7587 (1935).

[69] Hall, R. A., U. S. P. 2,081,117, May 18, 1937, to Colgate-Palmolive-Peet Co.; *Chem. Abs.,* **31,** 5111 (1937).

[70] Stockelbach, F. E., U. S. P. 2,041,874, May 26, 1936; *Chem. Abs.,* **30,** 5000 (1936).

[71] Risler, J., U. S. P. 1,779,891, Oct. 28, 1930; *Chem. Abs.,* **25,** 174 (1931).

[72] French P. 770,912, Sept. 24, 1934, to I. G. Farbenind. A.-G.; *Chem. Abs.,* **29,** 892 (1935); British P. 435,811, Sept. 30, 1935.

[73] Issermann, S., Ohlsson, E., and Orelup, J. W., U. S. P. 2,102,712, Dec. 21, 1937; *Chem. Abs.,* **32,** 1410 (1938).

[74] Jordan, A., German P. 652,929, Nov. 10, 1937; *Chem. Abs.,* **31,** 1410 (1938).

[75] See Hazen, H. H., *Am. J. Nursing,* **38,** 791 (1938).

[76] Schwarz, H., *Seifensieder-Ztg.,* **64,** 518 (1937); *Chem. Abs.,* **31,** 6413 (1937).

[77] Merkel, E., and Wiegand, C., U. S. P. 2,104,492, Jan. 4, 1938; *Chem. Abs.,* **32,** 1869 (1938).

[78] Urbach, E., and Kral, F., *Klin. Wochschr.,* **16,** 960 (1937); *Chem. Abs.,* **31,** 8015 (1937).

Secerov [79] found that after five to forty hours of exposure to ultraviolet rays the hair of a white guinea pig became yellow. In rats the production of alopecia by thallium is said to be reduced or retarded by the action of ultraviolet rays, which also accelerate the regeneration of hair in the bald spot.[80]

Light may be concerned in the production of argyria, the deposition of silver in the skin, after internal administration of silver salts.[81] The same may also be true of chrysiasis, the deposition of gold, after prolonged treatment with the gold compound, Sanocrysin.[82]

Metabolism and Circulation

Only after very intense irradiation is the general body temperature elevated. When a sufficient amount of tissue damage has been done there may be a fever similar to that which follows the injection of protein destruction products. The effects of irradiation upon the basal metabolism are of little importance. During irradiation it may be increased by as much as 18 per cent, but it quickly returns to normal on the cessation of irradiation and remains unchanged during the erythema state.[83] Harris [84] found that ultraviolet radiation exerts a stimulant action on the gaseous metabolism of small animals and on the movements of the isolated stomach of the frog. This stimulus he believed to be completely annulled by visible radiation, the antagonism being physiological rather than physical. He also stated that exposure of an animal to the mixed radiations of a powerful source of light depresses its heat production, the depression being greater in pigmented animals than in albinos.

No effect on the basal metabolism of healthy men, mice or rats could be observed by Campbell [85] on exposure to a mercury-vapor lamp, or to its rays when filtered through Uviol glass, or to visible light. On the other hand, Sonne [86] found that the oxygen consumption of the chrysalids of the meal worm could be accelerated by light energy of from 1 to 200 gm. cal. per minute per sq. cm. The shorter wave-lengths had the greater effect. There was an increase of about 40 per cent during an exposure of 45 minutes to the unfiltered light of a Kromayer lamp, of about 20 per cent when a glass filter was used and of about 10 per cent when both a glass filter and a methylene blue filter were used. Yellow light had no influence on the respiratory metabolism. An increase of about 15 per cent persisted for several hours after irradiation by unfiltered light, but there were no after effects following irradiation by filtered light which eliminated the central band of ultraviolet frequencies.

Crofts [87] observed a 14-per cent fall in oxygen consumption in canaries on ultraviolet irradiation. This was followed two to six days after the exposure by a rise of 21 per cent. In normal rabbits and in six normal human subjects, no effects were noted which could be ascribed to the irradiation. Lippmann and Völker [88] found a slight increase in human subjects (10 to 18 per cent) but the metabolism

[79] Secerov, S., *Compt. rend.*, **158**, 1826 (1914).

[80] Buschke, A., and Vasarhelyi, J., *Klin. Wochschr.*, **11**, 678 (1932); *Chem. Abs.*, **27**, 779 (1933).

[81] Lenartowicz, J., and Jalowy, B., *Arch. Dermatol. Syphilol.*, **9**, 483 (1938); *Chem. Abs.*, **32**, 9266 (1938).

[82] Schneidewind, A., Albertal, M., and Trajtenberg, S., *Rev. asoc. med. argentina*, **52**, 792 (1938); *Chem. Abs.*, **32**, 9264 (1938).

[83] See, however, Kestner, O., Peemöller, F., and Plaut, R., [*Klin. Wochschr.*, **2**, 2108 (1923)], Kestner, O., Peemöller, F., and Schadow, H., [*Pflüger's Arch. ges. Physiol.*, **217**, 473 (1927)], and Kestner, O., and Schadow, H., [*Ibid.*, **217**, 492 (1927)] for a different point of view.

[84] Harris, D. T., *Proc. Roy. Soc.*, **98B**, 171 (1925).

[85] Campbell, J. A., *Proc. Roy. Soc.*, **99B**, 451 (1926).

[86] Sonne, C., *Acta Radiol. Skand.*, **5**, 419 (1926); *Chem. Abs.*, **21**, 1139 (1927).

returned to normal shortly after the irradiation was discontinued. The administration of iodine did not increase nor prolong the effect. Mělka [89] found a 14- to 47-per cent increase in oxygen consumption in persons exposed to the noon July sun. It has been stated [90] that in certain persons the quartz mercury lamp may produce a fall in total metabolism. This is the effect when the blood bilirubin is high, or if the skin is abundantly pigmented or if there has been an excessive consumption of buckwheat. The effect is ascribed to photosensitization.[91]

Pincussen [92] found solar irradiation to stimulate the protein metabolism of rabbits as shown by an increased nitrogenous excretion. This was still further increased by sensitizers such as dyestuffs and potassium iodide. Liebesny [93] fed two dogs on a constant diet of horse tripe and found exposure to the ultraviolet rays from a mercury-vapor lamp to cause an appreciable reduction in the volume of urine and in the total nitrogen, creatinine, and neutral sulfur content. Yoshine [94] observed a slight rise in the positive nitrogen balance of irradiated dogs if the exposure was short, but this changed to a negative balance when longer exposures were given. Longer periods of irradiation led to disturbances in the absorption of nitrogenous substances in the intestine and to a refusal of food. The slight irradiation which caused the positive balance consisted of a one-hour irradiation on each of eight consecutive days. The severe irradiation consisted of four hours of exposure daily. Fontès and Yovanovitch [95] believed that the exclusion of light decreases the nitrogen metabolism nearly to the level attained during sleep, and that the decrease during sleep while exposed to light is less than that in sleep in darkness. On the other hand, Mayerson, Gunther and Laurens [96] found that in adult dogs transient increases in the endogenous nitrogen metabolism, and in the absorption of calcium and phosphorus from the intestine, resulted when the animals were taken from light to darkness or *vice versa*. It was concluded that any deviation from the usual supply of radiant energy acts as a transient stimulus to these metabolic processes.

Exposure of normal men, women and children to summer sunlight or to a carbon arc causes an increase in creatinine excretion during the period of irradiation, according to Eichelberger,[97] but for a few hours subsequently there is a decreased excretion. No effect was observed on the excretion of creatine or on the basal metabolic rate.

Nothhaas and Schadow [98] studied the nitrogen balance of a series of children, first in Hamburg and again at the sea-shore. In spite of inadequate diet, nitrogen retention is increased under the latter conditions, even although the weight may not be increased. Other children remaining in Hamburg and treated with artificial ultraviolet light showed irregular effects, but in some a positive nitrogen balance was obtained.

[87] Crofts, E., *Am. J. Hygiene*, **8**, 1014, 1024 (1928); *Chem. Abs.*, **23**, 2466 (1929).

[88] Lippmann, A., and Völker, H., *Klin. Wochschr.*, **7**, 213 (1928); *Chem. Abs.*, **22**, 1168 (1928).

[89] Mělka, J., *Bratislava Lekarske Listy*, **6**, 50 (1926); *Chem. Abs.*, **22**, 4137 (1928).

[90] Mason, D. H., and Mason, H. H., *Arch. Int. Med.*, **39**, 317 (1927); *Chem. Abs.*, **21**, 2303 (1927).

[91] Summarizing lectures on the effect of light on metabolism have been given by Pincussen, L., *Strahlentherapie*, **48**, 308 (1933) and by Mangold, E., *Ibid.*, 319.

[92] Pincussen, L., *Biochem. Z.*, **150**, 36 (1924).

[93] Liebesny, P., *Z. Physik. Diatet. Therap.*, **24**, 182 (1920); *Chem. Abs.*, **15**, 2905 (1921).

[94] Yoshine, S., *Strahlentherapie*, **18**, 201 (1924); *Chem. Abs.*, **20**, 1430 (1926).

[95] Fontès, G., and Yovanovitch, A., *Compt. rend. soc. biol.*, **93**, 269 (1925); *Chem. Abs.*, **19**, 3527 (1925).

[96] Mayerson, H. S., Gunther, L., and Laurens, H., *Am. J. Physiol.*, **75**, 399, 421 (1926).

[97] Eichelberger, M., *J. Biol. Chem.*, **69**, 17 (1926).

[98] Nothhaas, R., and Schadow, H., *Jahrb. Kinderheilk.*, **127**, 1 (1930); *Chem. Abs.*, **26**, 763 (1932); see also Ferri, U., *Pediatria Rev.*, **35**, 1110 (1927); *Chem. Abs.*, **22**, 2599 (1928).

Pincussen, Bayerl, Brück, Görne and Rothmann,[99] believed irradiation of pigs with infrared, visible and ultraviolet light to cause, in general, increased elimination of total nitrogen and of purines.

The discrepancies in these reports are due, in part, to the differences in the subjects and the nature and duration of the exposures, and in part to the time following irradiation when the observations were made. It is apparent that no very marked changes occur in most individuals. Lehmann and Szakáll[100] found the effect of ultraviolet irradiation at weekly intervals lowered the basal metabolism of six human subjects 10 to 15 per cent, and increased the capacity for work up to 60 per cent, while decreasing the oxygen debt. The various effects were believed to be very similar to the results attained by training. When an ultraviolet-impervious screen was interposed without the knowledge of the subject, the increased capacity for work did not occur. Another subject showed a loss of weight, a lowering of the basal metabolism and a rise in the respiratory quotient when treated, in contrast to a daily fall in weight and a slight increase in the alkali reserve when not treated.

The pulse rate is usually unaltered, and circulatory effects are not prolonged. The blood pressure is usually lowered, but the circulatory changes are not remarkable. As early as 1905, Hasselbalch[101] observed decreases of from 8 to 10 per cent in blood pressure which lasted for several months following the application of massive doses of the rays from a carbon arc. He ascribed the effects to the cutaneous hyperemia. The most thorough recent studies are by Laurens and Mayerson.[102]

Reed[103] showed that irradiation of the eyes of anesthetized dogs caused a considerable drop in the arterial blood pressure, but there was no evidence for the liberation of a depressor substance into the blood. The effect could not be ascribed solely to nervous factors since it was not abolished by bilateral section of the vagi and section of the optic nerve. The effect was attributed to a direct action upon the blood, since similar effects resulted from the irradiation of the blood circulating through a quartz tube interposed in the carotid artery. The light used was that of a carbon arc and the results were the same when either the infrared rays or the ultraviolet rays of wave-lengths shorter than 3300A had been removed. The coagulation time of the blood was increased, and it was necessary to use intravenous injections of heparin to prevent coagulation of the blood in the circulation. There were no marked effects upon the hemoglobin content or upon the red blood cells, but the white cells decreased, with a relative lymphocytosis and an absolute lymphopenia.[104]

Rowinski[105] could detect no change in the vasoconstricting power of the blood serum of patients who had taken sea or sun baths. Sidoli[106] found that irradiation of the blood serum *in vitro* caused a decrease in its power of vasoconstriction proportional to the intensity of the radiation employed. This he ascribed to a

[99] Pincussen, L., Bayerl, V., Brück, E., Görne, J., and Rothmann, A., *Strahlentherapie,* **45,** 401 (1932); *Chem. Abs.,* **27,** 4836 (1933).

[100] Lehmann, G., and Szakáll, A., *Arbeits. Physiol.,* **5,** 278 (1932); **6,** 84 (1932); *Chem. Abs.,* **28,** 2396 (1934).

[101] Hasselbalch, K. A., *Skand. Arch. Physiol.,* **17,** 431 (1905); *Berlin Klin. Wochschr.,* **44,** 1247 (1907).

[102] Laurens, H., and Mayerson, H. S., *Am. J. Physiol.,* **84,** 524 (1928).

[103] Reed, C. I., *Am. J. Physiol.,* **74,** 511, 518, 525 (1925); bibliography of effect of light on blood pressure is included.

[104] Reed, C. I., *Archiv. Phys. Ther. X-Ray, Radium,* **8,** 108 (1927).

[105] Rowinski, P., *Boll. soc. ital. biol. sper.,* **6,** 818 (1931); *Chem. Abs.,* **26,** 1966 (1932).

[106] Sidoli, E., *Arch. sci. biol. ital.,* **19,** 443 (1934); *Chem. Abs.,* **29,** 3359 (1935).

decrease of the adrenalin present in the serum. During irradiation *in vivo,* however, there is no such change.[107]

Effects on the Blood

The effect of a general irradiation of the body upon the formed elements of the blood is not remarkable, at least in normal individuals. The literature is extensive but frequently contradictory. To summarize the individual papers would leave the reader with a feeling of confusion, and would consume much space. Instead, only a few of the more significant conclusions which it seems possible to draw will be stated, together with references to a few papers from which, as well as from the special works cited earlier in the chapter, the reader may obtain more complete references to other work.[108]

Several writers have found no changes induced in the cell count by irradiation.[109] It seems to be established that normal men or other animals can live on an ample balanced diet for prolonged periods during which sunlight or artificial illumination is absent or much reduced without the production of an anemia.

Hardy[110] tabulated the data of some 45 investigators. Eleven reported no change in the red cells, while 18 reported an increase and only two a decrease. There were wide differences in the species of animal used, and in the conditions of irradiation, sources, energies and wave-lengths. Her own conclusions, after a careful weighing of the available evidence, were that a normal red cell count may be very slightly increased and a low one raised to normal by daily irradiations. Most observers have reported a leucocytosis after ultraviolet irradiation, but there is much variation both in the amount of change in the total white cell count and in the differential count.

One reason for the variations in the results of different observers is that, as pointed out by Balderrey and Barkus,[111] the primary effect of irradiation is a vasodilatation followed by a diffusion of tissue fluid into the blood stream, resulting in dilution and increased blood volume. When the irradiation is long-continued or frequently repeated, this effect may be counteracted by vasoconstriction and blood concentration. Thus, alterations in blood concentration may tend to mask any real variations in the numbers of the various formed elements. At different periods during and after irradiation, these opposing effects may predominate to varying degrees and cause confusion. Mayerson and Laurens[112] found a single exposure to carbon arc radiations to produce a temporary increase in the plasma volume of the blood of dogs, amounting to 6 to 37 per cent, and followed by recovery to normal within five hours. Repeated exposures caused an increase in the number of red cells of 10 to 19 per cent, maintained for three to six weeks after the final irradiations. The color, volume and saturation indexes showed that the cells in the post-irradiation period were usually smaller and less saturated than before irradiation. The platelets dropped in number and volume by 35 per

[107] See also Johnson, J. R., Pollock, B. E., Mayerson, H. S., and Laurens, H., *Am. J. Physiol.,* **114,** 594 (1936).

[108] For a review, see Furniss, A., *Brit. J. Actinother.,* **5,** 187 (1930); an alteration in the absorption spectrum of hemolyzed blood was not found following irradiation of the subject by Varshaver, G. S., *Arch. sci. biol. (U.S.S.R.),* **41,** No. 2, 31 (1936); *Chem. Abs.,* **31,** 7905 (1937).

[109] Jaulmes, C., *Compt. rend. soc. biol.,* **92,** 268 (1925); Koopman, J., *Deut. med. Wochschr.,* **50,** 277 (1924); *Chem. Abs.,* **18,** 2197 (1924); Tataranu, I., *Compt. rend. soc. biol.,* **97,** 1736 (1927); *Chem. Abs.,* **22,** 1799 (1928); Sinclair, R. D., *Sci. Agr.,* **13,** 737 (1933) (in pigs); *Chem. Abs.,* **23,** 3955 (1929).

[110] Hardy, M., *Am. J. Hygiene,* **7,** 811 (1927); **8,** 1024 (1928).

[111] Balderrey, F. C. and Barkus, O., *Am. Rev. Tuberculosis,* **9,** 107 (1924).

[112] Meyerson, H. S., and Laurens, H., *Am. J. Physiol.,* **86,** 1 (1928); *J. Nutrition,* **3,** 465 (1931); *Chem. Abs.,* **25,** 2461 (1931).

cent during the irradiation, with recovery usually within five hours after each exposure. Leucocytosis resulted from moderate irradiation but markedly low levels in the white blood cell counts followed strong excessive exposures.[113] Excessive irradiation also appeared to destroy red blood cells. In experimental anemias of animals, there seems to be a more rapid restoration of the red cells after ultraviolet irradiation, although too much or too frequent irradiation seems to be definitely harmful.[114] Although the number of red blood cells and the number of reticulocytes increased as a result of irradiation by the flaming carbon arc, the corpuscular volume and the corpuscular hemoglobin did not. In fact, the hemoglobin was practically unaltered. On the other hand, in hemolytic anemia produced by phenylhydrazine, a regeneration of hemoglobin was observed.[115] In nutritional anemias, as the milk anemias, results with the carbon arc were negative, but with the quartz mercury arc, Foster[116] obtained some evidence of a beneficial effect. The number, size, and saturation of the red cells were increased.

Cramer and Drew found light to act as a stimulus to the formation of blood platelets. This has been confirmed by others, including Hardy,[117] Steiner and Gunn,[118] and, in new-born infants, Sanford.[119]

Friedlander and Wiedemer[120] note that in healthy persons the reticulocytes (young red cells) increase in the spring months as contrasted with the count during the winter. They attribute this to an increase in ultraviolet rays from the sun. Seyderhelm,[121] has claimed that dog blood upon ultraviolet irradiation develops the property of causing a sudden outpouring of erythrocytes into the blood of dogs made artificially anemic by saponins. The active substance is associated with the stroma of the irradiated red cells. Normal blood contains small quantities of this active substance. Similar results were obtained in human subjects upon the intramuscular injection of irradiated human cells, the reticulocytosis reaching its maximum one to five hours after the injection. The results in pernicious anemia are not as permanent as those obtained with liver. According to Zaepffel,[122] rapid blood regeneration may be produced in anemic rabbits or patients by the oral administration of solutions obtained by digesting red blood cells with pancreatin followed by exposure to strong ultraviolet light. The final product contained histidine, tryptophane and hematin.

Goldberg[123] found parenteral administration of solutions obtained by irradiating copper or iron plates in water with ultraviolet rays to accelerate the regenerative processes in rabbits made anemic by bleeding. The local anaphylactic reaction is depressed by the use of ultraviolet-treated metals. These materials also produce capillary dilatation in frogs when injected subcutaneously.[124]

[113] See also Clark, J., *Physiol. Rev.*, **2**, 285 (1922); Koopman, J., *Deut. med. Wochschr.*, **50**, 277 (1924).

[114] Hobert, H., *Klin. Wochschr.*, **2**, 1213 (1923); *Chem. Abs.*, **17**, 3893 (1923).

[115] Mayerson, H. S., and Laurens, H., *J. Nutrition*, **4**, 351 (1931); see also Kasatkin, E. V., and Bogdanova, G. P., *Arch. sci. biol. (U.S.S.R.)*, **40**, No. 1, 49 (1936); *Chem. Abs.*, **37**, 6679 (1937).

[116] Foster, P. C., *J. Nutrition*, **4**, 517 (1931); *Chem. Abs.*, **26**, 3008 (1932).

[117] Hardy, M., *loc. cit.*

[118] Steiner, P. E., and Gunn, F. D., *Arch. Path.*, **11**, 241 (1931); *Chem. Abs.*, **25**, 4563 (1931).

[119] Sanford, H. N., *Am. J. Diseases Children*, **83**, 50 (1927).

[120] Friedlander, A. and Wiedemer, C., *Arch. Int. Med.*, **44**, 209 (1929).

[121] Seyderhelm, R., *Klin. Wochschr.*, **11**, 628 (1932); *Chem. Abs.*, **26**, 4856 (1932).

[122] Zaepffel, H., *Bull. acad. med.*, **113**, 679 (1935); *Chem. Abs.*, **30**, 7657 (1936).

[123] Goldberg, I. M., *Acta. Med. Skand.*, **85**, 136, 147 (1935); Goldberg, I. M., and Boudyline, V. G., *Ibid.*, 147.

[124] Boudyline, V. G., *Acta. Med. Skand.*, **86**, 88, 95 (1935); see also Griegel, C. R., *Klin. Wochschr.*, **45**, 705 (1936).

Toyoda[125] finds that irradiation of rabbits produces thrombocytogenesis, and a histamine-like substance is believed to be produced in the blood, which acts on the spleen. When the irradiation is repeated more than about five times, thrombopenia results. Such thrombopenic rabbits will again show thrombocytogenesis if a fresh spleen is grafted. When the spleen of a thrombopenic rabbit is grafted to normal splenectomized rabbits, irradiation produces no change in thrombocytes.

According to Tokumitu and Toyota[126] the number of platelets increases in the normal rabbit within an hour after irradiation with rays between 3130 and 3900A, and returns to normal after two to four hours. It does not increase in splenectomized rabbits. In parathyroidectomized rabbits, the increase is more marked than in normal ones. These authors suggest that there exists a specific splenic hormone, which controls thrombocytosis and that its liberation from the spleen is controlled by a histamine-like substance produced in the skin during irradiation. In splenectomized animals the thrombocytosis on irradiation could be observed if normal spleen had been grafted into the animals.

Koh[127] noted that when a rabbit has been irradiated by these wave-lengths for an hour, erythrocytes and hemoglobin are increased in the ear vein within five hours, but they are decreased in the liver and spleen. No reticulocyte increase was noted in any veins. The effect is not due to a regeneration of the corpuscles but rather to an alteration in their distribution. This polyerythemia of the ear veins can be produced in animals from which the thyroid, but not in those from which the spleen, has been removed. It is suggested that the thyroid has a hormone which antagonizes the splenic hormone and that the former is concerned with the redistribution of erythrocytes after the irradiation. Carnielli reports that irradiation of rats and guinea pigs produces a considerable increase of the oxidase in the leucocytes.[128]

Recently there have been many determinations of the ultraviolet absorption of blood, its plasma and serum, and attempts have been made to correlate variations in the absorption spectra with diseased conditions. These are not discussed, since they have not as yet led to any very useful results and because our subject matter is limited to effects dependent upon the occurrence of photochemical processes.

Macht and Blackman[129] noted that animals poisoned with carbon monoxide and exposed to ultraviolet rays recovered more quickly than controls poisoned to the same degree and kept in darkness. This was attributed to the photodissociation of the carbon monoxide-hemoglobin. Estler,[130] however, was unable to verify these observations and concluded that the *in vitro* dissociation of the complex with hemoglobin had no counterpart *in vivo*. Gorkin finds the dissociation can be affected by daylight, but not by ultraviolet light.[131]

Harris[132] finds that irradiation of blood causes it to give up oxygen at high oxygen tensions and to take it up at low tensions. Both effects are irreversible in darkness. At about 15 mm. tension of oxygen there is gaseous equilibrium. The taking up of the oxygen by blood in ultraviolet light he believed to be a property of the plasma. In the presence of traces of certain sensitizing substances, iron chloride, dyes, and especially hematoporphyrin and chlorophyll, the velocity of the photoöxidation of plasma may be increased up to a hundred fold. The accelerating effect of hematoporphyrin is unaffected by the addition of sodium cyanide. It was noted in Chapter 34 that certain proteins and the aromatic amino- acids undergo a similar photoöxidation. Krebs[133] finds that light affects the hemin

[125] Toyoda, G., *J. Chosen Med. Assoc.*, **22**, 673 (1932); **26**, 856, 1017 (1936); *Chem. Abs.*, **31**, 1869 (1937).

[126] Tokumitu, Y., and Toyota, G., *Trans. Japan. Path. Soc.*, **21**, 191 (1931); *Chem. Abs.*, **26**, 6003 (1932).

[127] Koh, M., *J. Chosen Med. Assoc.*, **22**, 775 (1932); *Chem. Abs.*, **27**, 2197 (1933).

[128] Carnielli, P., *Biochem. terap. sper.*, **25**, 1 (1938); *Chem. Abs.*, **32**, 4183 (1938).

[129] Macht, D. I., and Blackman, S. S., Jr., *J. Pharmacol.*, **23**, Proc. 142 (1924); *Chem. Abs.*, **18**, 3228 (1924).

[130] Estler, W., *Arch. Hyg. Bakt.*, **115**, 152 (1936); *Chem. Abs.*, **30**, 3096 (1936).

[131] Gorkin, Z. D., *J. Physiol (U.S.S.R.)*, **22**, 329 (1937); *Chem. Abs.*, **32**, 9103 (1938).

[132] Harris, D. T., *Biochem. J.*, **20**, 280, 271 (1926).

[133] Krebs, H. A., *Biochem. Z.*, **193**, 347 (1928).

catalysis of the oxidation of cysteine to cystine by molecular oxygen in the same way that it affects the respiration of living systems.

The oxygen consumption of red blood cells (and also of yeast cells) in Tyrode's solution at pH 7.2 may be increased by 50 per cent during irradiation by ultraviolet light, according to Surányi and Vermes.[134] Cyanide irreversibly inhibits both the normal and the increased respiration.

Hemolysis. Suspensions of red blood cells are slowly hemolyzed by visible light.[135] Meyerstein[136] found human cells which in physiological salt solution were hemolyzed in 13 to 14 days in darkness, hemolyzed in 5 to 6 days in light. Radiations of wave-lengths less than 2700A are more effective, according to Koeppe.[137] Hausmann and Sonne[138] found it possible to sensitize the cells to the longer wave-lengths of the ultraviolet by means of hematoporphyrin. The effect is then most marked at 3130A. *In vivo* this effect could not be demonstrated. Löhner[139] found arsenious acid to sensitize red blood cells to either visible or ultraviolet light. Fabre and Simonnet[140] state that cholesterol-free lecithin, if irradiated in the presence of hematoporphyrin by ultraviolet light, undergoes a change by which it acquires a greater hemolytic power than it can attain on unsensitized irradiation.

During the irradiation of normal persons a gain in fecal urobilin was observed by Teplov and Mesheristkaya.[141] This was attributed to increased hemolysis. At the same time the production of red cells was stimulated, so that the total number of red cells and the hemoglobin content of the blood usually remained constant. In anemic subjects, the apparent regeneration of the blood is explained by an overcompensation which causes the rate of the production of blood to exceed the rate of hemolysis. At the conclusion of the treatment, the rate of hemolysis sinks rapidly to normal, and the overproduction of red cells also subsides.

Farkas and Tangl[142] had noted, on the contrary, that in dogs, unless splenectomized, ultraviolet irradiation inhibits the passing out of their blood pigment.

Ward[143] has claimed that the influenza bacillus when grown on blood-agar plates is unable to produce hemolysis if incubated in darkness. If it is then exposed to sunlight or artificial light, it shows a definite hemolysis after a time which depends upon the intensity of the light.

The permeability of erythrocytes to water-soluble substances, such as glycerol, glucose, etc., is said to be increased by light.[144] The spectral distribution of the efficiency of radiation in decreasing the stability of the red cells corresponds very closely to that of the absorption of radiations by oxyhemoglobin.[145] This suggests that the effect is exerted upon the hemoglobin rather than upon the colorless cell membrane.

Although hematin and hemochromogen are not altered by sulfur dioxide in

[134] Surányi, G., and Vermes, M., *Magyar Orvosi Arch.*, **30**, 585 (1929); *Chem. Abs.*, **25**, 2162 (1931).
[135] Hausmann, W., and Loewy, A., *Biochem. Z.*, **173**, 1 (1926); Earle, W. R., *J. Exptl. Med.*, **48**, 457, 667, 583 (1928); Lepeschkin, W. W., *Science*, **73**, 568 (1931).
[136] Meyerstein, *Klin. Wochschr.*, **7**, 2244 (1928); *Chem. Abs.*, **23**, 1438 (1929).
[137] Koeppe, H., *Arch. Kinderheilk.*, **79**, 109, 198 (1926).
[138] Hausmann, W., and Sonne, C., *Strahlentherapie*, **25**, 174 (1927).
[139] Löhner, L., *Biochem. Z.*, **186**, 194 (1927).
[140] Fabre, R., and Simonnet, H., *Compt. rend.*, **184**, 707 (1927).
[141] Teplov, I., and Mesheristkaya, R., *Deut. Arch. Klin. Med.*, **174**, 399 (1933); *Chem. Abs.*, **27**, 5347 (1933).
[142] Farkas, G., and Tangl, H., *Biochem. Z.*, **200**, 184 (1928); *Chem. Abs.*, **23**, 168 (1929).
[143] Ward, H. K., *J. Bacteriol.*, **15**, 51 (1928).
[144] Lepeschkin, W. W., *Protoplasma*, **18**, 243 (1933); *Chem. Abs.*, **27**, 3228 (1933).
[145] Lepeschkin, W. W., and Davis, G. E., *Protoplasma*, **20**, 188 (1933); *Chem. Abs.*, **28**, 1722 (1934).

darkness, when illuminated with this compound they lose iron and are converted into hematoporphyrin-like substances. These differ from Nencki's hematoporphyrin in their sulfur content and in their solubility, according to Zeynek and Kittel.[146] Under similar conditions, blood pigments also lose their iron and are converted into porphyrin-proteoses, containing varying amounts of more or less firmly bound proteins. Light sensitization of white mice by these products differs little from sensitization by Nencki's hematoporphyrin.

Vital staining in the red cells of frogs is said to be materially retarded by light rays of the shorter wave-length half of the visible spectrum.[147]

Falk and Reed[148] found that in blood directly irradiated *in vivo*, there is a small but definite decrease in the negative electrophoretic potential of the red cells.

Blood Sugar and Carbohydrate Metabolism. Frenkel-Tissot[149] believed, as a result of studies at high altitudes, that people with high blood sugar tend to have this decreased by irradiation by the sun or the mercury arc or by hyperthermia, although those with normal or low blood sugar values show a tendency for the sugar to be increased by the same treatments. Many subsequent observers have noted a depression of the blood sugar on irradiation.[150] Petersen and v. Oettingen[151] found that in dogs a short exposure was as effective as a longer one in causing a reduction in the amounts of sugar and chlorides in the lymph, an increase in the number of white cells in the blood, and in the volume and protein content of the lymph.

When blood is directly irradiated in quartz tubes *in vivo* by the method of Reed, in anesthetized dogs, the blood sugar is not affected.[152] Treatment of guinea pigs, cats and dogs with serum which had been previously irradiated in most cases reduced the elimination of sugar by the liver.[153]

Keeser[154] observed that rabbits placed in blue light and injected intravenously with glucose show a less pronounced and shorter hyperglucemia than those injected in daylight. Irradiation also causes an increased content of sugar in the skin. There is also a marked decrease of from 31 to 15 mg. per cent in the reduced glutathione content of the skin and a smaller decrease in that of the blood. Keeser[155] believes blue light to have a sympathicotonic and red light a vagotonic action.

Ogawa[156] found the reduced glutathione in both arterial and venous blood of irradiated rabbits to be decreased immediately after irradiation. After thirty to sixty minutes, however, it increased markedly. The same was true of the content of the oxidized form in arterial blood, but in the venous blood it increased immediately after the irradiation.

[146] Zeynek, R., and Kittel, S., *Z. physiol. Chem.*, **224**, 233 (1934); *Chem. Abs.*, **28**, 4079 (1934).
[147] Kedrovskiĭ, B., *Protoplasma*, **22**, 607 (1935); *Chem. Abs.*, **29**, 3362 (1935).
[148] Falk, I. S., and Reed, C. I., *Am. J. Physiol.*, **75**, 616 (1926).
[149] Frenkel-Tissot, H. C., *Deut. Arch. Klin. Med.*, **133**, 286 (1920); *Chem. Abs.*, **15**, 118 (1921).
[150] Pincussen, L., and Jacoby, D., *Biochem. Z.*, **195**, 449 (1928); Bloch, C. E., and Faber F., *Am J. Dis. Children*, **30**, 504 (1925); Rothmann, H., *Klin. Wochschr.*, **2**, 881 (1923); Pincussen, L., and Yakota, S., *Biochem., Z.*, **241**, 398 (1931); Pincussen, L., *Biochem, Z.*, **272**, 354 (1934); *Klin. Wochschr.*, **10**, 791 (1933); **11**, 1231 (1932); *Chem. Abs.*, **26**, 5612 (1932); *Strahlentherapie*, **51**, 537 (1934).
[151] Petersen, W. F., and v. Oettingen, W. F., *Arch. Exptl. Path. Pharmakol.*, **123**, 160 (1927); *Chem. Abs.*, **22**, 276 (1928).
[152] Reed, C. I., Payte, J. I., and Lackey, R. W., *Proc. Soc. Exptl. Biol. Med.*, **24**, 11 (1926).
[153] Holtz, P., *Arch. Ges. Physiol. (Pflüger's)*, **226**, 578 (1931); *Chem. Abs.*, **25**, 2194 (1931).
[154] Keeser, E., *Arch. Expt. Path. Pharmakol.*, **166**, 624 (1932) .
[155] See also von Deschwander, J., who attributes the results to increased insulin formation; [*Strahlentherapie*, **39**, 278 (1931); *Chem. Abs.*, **25**, 1886 (1931); *Strahlentherapie* **46**, 713 (1933); *Chem. Abs.*, **27**, 3489 (1933)].
[156] Ogawa, M., *J. Agr. Chem. Soc. Japan*, **13**, 81 (1937); *Chem. Abs.*, **31**, 3077 (1937).

Jona [157] gave progressively increasing daily irradiations to four normal persons and two diabetics for a month. In the normal persons there was a diminution in glucemia but no notable effect on the glucose tolerance or glycosuria. In the diabetics it was found that although both the glucemia and glycosuria were diminished, the general condition of the patients was adversely affected and the acetonuria increased.

Gorini [158] finds that small doses of ultraviolet rays enhance the glucose metabolism and large doses depress it. In infants and children, the blood sugar is increased by ten minutes and reduced by twenty minutes of irradiation or by the use of greater intensities, according to Ferri.[159] In alimentary hyperglucemia, the reaction is hastened by short and retarded by long exposures, but adrenalin hyperglucemia is always enhanced by irradiation. Ceruti [160] determined the glucemic titer before and after the irradiation of albino rats. In a group exposed to the direct rays of the mercury-vapor lamp for 15, 30 and 60 minutes, there was an average diminution of 10, 25 and 31 per cent respectively. In a group exposed with a Wood glass filter the values were 8, 13, and 18 per cent, and in a third group in direct sunlight, 6, 9 and 12 per cent.

Kallós and Kallós-Deffner [161] found that ultraviolet light lowered the fasting blood sugar and increased the sugar tolerance of rabbits which had been previously kept in darkness for a week.[162] On the other hand, Müller [163] found no difference in the blood sugar level of rabbits kept in darkness for two or three weeks from that of those kept in the light. Nor could a difference in the glucose tolerance be detected.

Ventral irradiation is said to be more effective than dorsal in producing a constant and progressive decrease in the blood sugar of rabbits by Benvenuto,[164] who did not succeed, however, in demonstrating an effect upon the glucose tolerance. Besides noting a decrease in the blood sugar which reaches its maximum at the height of the erythema, Marchionini and Hövelborn [165] found the blood diastase to be increased by ultraviolet irradiation.

Burge and Wickwire [166] find that the normal rate of utilization of glucose and galactose by *Paramecium caudatum* is depressed by ultraviolet irradiation. This effect is abolished by the addition of insulin to the medium and was thought to be due to the destruction of insulin in the living cells by the irradiation.

Pincussen and Jacoby [167] find the lactic acid content of the whole blood of rabbits to decrease by 20 to 30 per cent shortly after an irradiation. The content in the serum, however, increases. The authors suggest that during irradiation the permeability of the corpuscles may increase so as to permit the passage of a considerable part of their lactic acid into the serum. The glycogen of heart and muscle, if changed at all, decreases slightly, although the total carbohydrate increases considerably. It appears therefore, that irradiation causes a sparing of

[157] Jona, A., *Minerva Med.*, **II**, 757 (1933); *Chem. Abs.*, **28**, 1401 (1934).
[158] Gorini, P., *Pediatria Rivista*, **35**, 1110 (1927); *Chem. Abs.*, **22**, 2599 (1928).
[159] Ferri, U., *Riv. clin. pediatr.*, **25**, 217 (1927); *Chem. Abs.*, **22**, 619 (1928).
[160] Ceruti, G., *Boll. soc. ital. biol. sper.*, **3**, 30 (1928); *Chem. Abs.*, **22**, 2383 (1928).
[161] Kallós, P., and Kallós-Deffner, L., *Strahlentherapie*, **50**, 191 (1934); *Chem. Abs.*, **28**, 4772 (1934). See also Root, R. W., *Arch. Phys. Therapy, X-Rays, Radium*, **12**, 153 (1931); *Chem. Abs.*, **26**, 1648 (1932).
[162] See also Rothman, S., *Strahlentherapie*, **51**, 364 (1934); Pincussen, L., *Ibid.*, **53**, 7 (1934).
[163] Müller, R. W. J., *Biochem. Z.*, **276**, 416 (1935).
[164] Benvenuto, E., *Pediatria Riv.*, **43**, 675 (1935); *Chem. Abs.*, **30**, 4182 (1936).
[165] Marchionini, A., and Hövelborn, C., *Klin. Wochschr.*, **14**, 1387 (1935); *Chem. Abs.*, **30**, 2997 (1936).
[166] Burge, W. E., and Wickwire, G. C., *J. Biol. Chem.*, **72**, 827 (1927).
[167] Pincussen, L., and Jacoby, D., *Biochem. Z.*, **195**, 449 (1928).

sugar but it was uncertain whether this was due to a decreased breakdown of the sugar or to an increased formation of sugar from lactic acid. Later, however, Pincussen and Kawakami [168] stated that in the liver and muscles of irradiated animals there is an increase in glycogen at the expense of lactic acid. The glycocen : lactic acid ratio is raised 55 and 45 per cent in the liver and muscles, respectively, but in the heart the change does not exceed the experimental error. They believe the radiations to act in a manner similar to that of insulin.

By irradiating muscle extract before incubation, Stiven [169] has found it possible to increase the rate of lactic acid formation from glycogen. In one case the rate of lactic acid formation in the irradiated sample was three times that in the control. Irradiation leads also to alterations of the accumulation of the phosphoric ester. Brief irradiations resulted in an increase of the ester accumulation, but longer ones produced a decrease. The higher rates of lactic acid formation coincide with a decrease in the ester accumulation. In only one of thirteen experiments was the lactic acid formation decreased after a long irradiation, and in this case the accumulation of ester was almost completely inhibited.

Blood pH. During the first hour after irradiation, there is a transient blood acidosis in human subjects, according to Kroetz.[170] This amounts to a drop of about 0.3 to 0.7 in pH and is ascribed by Kroetz to introduction into the blood of the altered proteins or their disintegration products formed as a result of the irradiation. This phase is followed by a more permanent alkalosis reached about 24 hours after the exposure. In it, the blood pH is raised about 0.05 to 0.07 unit above normal. This is ascribed to shifts of bases from the tissues to the blood. During the stage of acidosis, the blood is hydrated, but in the later stages the serum becomes more concentrated. In the early acidosis, the respiratory center is stimulated and there may be some hyperventilation. The alteration of the ionic equilibrium in the serum of the irradiated individual is summarized as an increase in the ratio $K^+ \times (H_2PO_4' + HPO_4'') / Ca^{++}$. Refractometric measurements revealed an alteration in the nature of the serum proteins. The early increase in blood acidity was also obtained as a result of the *in vitro* irradiation of blood. Hoeber [171] found ultraviolet light to render horse serum more acid. On the other hand, Moran and Reed [172] found irradiation of dog blood *in vivo* to fail to produce any constant effect on the carbon dioxide combining power.

According to Balderrey and Barkus [173] exposure of the human body to sunlight increases the alkalinity of the blood. The amount of pigmentation present has a direct influence on the change of the blood reaction, the greater the amount of pigmentation the more marked being the change in the blood pH. In their experiments, the effects were probably to be attributed predominantly to radiations of the visible spectrum. Variations in the intensity of the light materially influenced its effects on the blood reaction.

In earlier studies, Ederer [174] determined the influence of the light of a quartz lamp upon the alveolar carbon dioxide tension of man. The results varied with the

[168] Pincussen, L., and Kawakami, T., *Biochem Z.*, **208**, 185 (1929); Pincussen, L., *Arch. Phys. Therapy, X-Ray, Radium*, **18**, 750 (1937); *Chem. Abs.*, **32**, 4615 (1938).
[169] Stiven, D., *Biochem. J.*, **24**, 172 (1930).
[170] Kroetz, C., *Biochem. Z.*, **151**, 146, 449 (1924).
[171] Hoeber, R., *La Med. Germano-Hispano Amer.*, **1**, 113 (1923); *Physiol. Abs.*, **10**, 61; *Chem. Abs.*, **19**, 3115 (1925); see also Frontali, G., *Rev. Clin. Pediatr.*, **25**, 661 (1927); *Chem. Abs.*, **23**, 1657 (1929). There is a slight decrease in total nitrogen and albumin nitrogen and an increase in the globulin nitrogen, according to Murayama, M., *J. Oriental Med.*, **34**, 79 (1936); *Chem. Abs.*, **31**, 5820 (1937).
[172] Moran, W. H., and Reed, C. I., *Proc. Soc. Exptl. Biol. Med.*, **24**, 179 (1926).
[173] Balderrey, F. C., and Barkus, O., *Am. Rev. Tuberculosis*, **9**, 107 (1924).
[174] Ederer, S., *Biochem. Z.*, **132**, 103 (1922); *Chem. Abs.*, **17**, 303 (1923).

dosage administered. Weak stimulation had no effect. Radiations of medium intensity increased the carbon dioxide tension but strong irradiation lowered it. The effects appeared to be independent of the skin erythema. The hypercapnic effect was considered to be hematogenous and not of central origin. This interpretation was based upon a belief, then undemonstrated, in a probable increase in the alkalinity of the blood, a decrease in the acid products of metabolism and a change in the colloidal state of the blood proteins.

Glass [175] observed for two to four hours after intense ultraviolet treatment, a change in the chlorine distribution in the blood, which was regarded as an indication of a shift in the acid-base equilibrium in the blood toward an acidotic condition. This sometimes persisted for 24 hours.

The analysis of urine samples during an hour after a single irradiation failed to indicate to Essinger and György [176] any shift in the acid-base equilibrium. The serum calcium was slightly decreased.

Iancou and Iana [177] determined the pH of the blood serum of eleven nursing mothers at the beginning, middle and end of a period of irradiation of the mammary glands. In seven, it rose appreciably, in one it remained constant, in two it at first dropped slightly and then returned to its initial value and in one suffering from an infection it dropped very slightly. In six cases the calcium content rose appreciably and in the other five it dropped slightly. The action on the nurslings was even less pronounced, unstable and inconstant. Lenzi [178] believes irradiation to cause no change in the blood pH.

The effects of general body irradiation upon other features of the blood composition have been frequently studied. In normal subjects, no very pronounced changes in phosphorus in its various forms, chlorine, magnesium, calcium, sodium or potassium have been found. Slight positive or negative variations may be produced at various periods during or after irradiation, but rarely have marked changes been observed.[179]

Frontali [180] noted an increase in the inorganic phosphorus of serum which had been irradiated fifteen to sixty minutes by a mercury arc. Sacchi [181] observed a decrease in the phosphatase content of the bones of rats kept in darkness, which could be restored to normal by exposing them to direct sunlight for a week.

In the *in vivo* irradiation of blood streaming through a quartz tube interposed in the circulation, Reed and Tweedy [182] found no immediate changes in the blood

[175] Glass, J., *Biochem. Z.*, **231**, 45 (1931); *Chem. Abs.*, **25**, 2160 (1931).

[176] Essinger, R., and György, P., *Biochem. Z.*, **149**, 344 (1924).

[177] Iancou, A., and Iana, I., *Bull. soc. péd.*, **30**, 76 (1932); *Chem. Abs.*, **27**, 3729 (1933).

[178] Lenzi, F., *Biochim. terap. sper.*, **23**, 118 (1936); *Chem. Abs.*, **30**, 6018, 6772 (1936).

[179] Lodenkämper, H. *Balneologie*, **1**, 438 (1934); *Chem. Abs.*, **31**, 3948 (1937); Kroetz, C., *Biochem. Z.*, **151**, 449 (1924); Malczynski, S., *Compt. rend. soc. biol.*, **113**, 1297 (1923); *Chem. Abs.*, **27**, 5345 (1933); Pincussen, L., and Makrineos, I., *Biochem. Z.*, **161**, 61, 67 (1925); Mayerson, H. S., Gunther, L., and Laurens, H., *Proc. Soc. Exptl. Biol. Med.*, **22**, 469 (1925); Bomskov, C., and von Rose, M., *Klin. Wochschr.*, **10**, 1956 (1931); *Chem. Abs.*, **26**, 2495 (1932); Malczynski, S., Borsiewicz, A., and Toczyski, T., *Compt. rend. soc. biol*, **108**, 165 (1931); *Chem. Abs.*, **26**, 2754 (1932); von Rose, M., *Z. Kinderheilk*, **54**, 236 (1933); *Chem. Abs.*, **27**, 2985 (1933); Egidi, E., and Rowinski, P., *Boll. soc. ital. biol. sper.*, **9**, 118 (1934); *Chem. Abs.*, **28**, 3746 (1934); Stiemens, H., and Heringa, G., *Nederland. Tijdschr. Geneeskund.*, **77, II**, 1635 (1933); *Chem. Abs.*, **28**, 2732 (1934); Brown, W. H., and Howard, M., *J. Exptl. Med.*, **49**, 103 (1929); Fairhall, L. T., *Am. J. Physiol.*, **84**, 378 (1928); Maynard, L. A., Goldberg, S. A., and Miller, R. C., *Proc. Soc. Exptl. Biol. Med.*, **22**, 494 (1925); Orr, J. B., Magee, H. E., and Henderson, J. M., *J. Physiol*, **70**, *Proc.* 25 (1924); Howe, M. G., and Medlar, E. M., *Am. Rev. Tuberculosis*, **10**, 408 (1924); Moritz, A. R., *J. Biol. Chem.*, **64**, 81 (1925); Cheymol, J., and Quinquaud, A., *J. pharm. chim.*, **16**, 233 (1932); *Chem. Abs.*, **27**, 1901 (1933); Pincussen, L., *Biochem. Z.*, **182**, 359 (1927).

[180] Frontali, G., *Riv. Clin. Pediatra*, **25**, 661 (1927); *Chem. Abs.*, **23**, 1657 (1929); also De Toni, G., and Stancati, A., *Boll. soc. ital. biol. sper.*, **4**, 165 (1929); *Chem. Abs.*, **23**, 3721 (1929); Careddu, G., *Biochim. terap. sper.*, **18**, 109 (1931); *Chem. Abs.*, **25**, 4015 (1931).

[181] Sacchi, U., *Boll. soc. ital. biol. sper.*, **9**, 94 (1935); *Chem. Abs.*, **29**, 4781 (1935).

[182] Reed, C. I., and Tweedy, W. R., *Am. J. Physiol.*, **76**, 54 (1926).

calcium. No effects upon the diffusibility of the serum calcium could be observed to follow either the irradiation of an animal or of its serum directly, by Moritz.[183] The addition of calcium chloride to rabbit serum, previously irradiated either *in vivo* or *in vitro*, is said to depress its electrical conductivity; the effect is not observed in the absence of the preceding irradiation.[184]

In marked contrast to the observations upon normal subjects are the results obtained in rachitic animals discussed in Chapter 38. The irradiation of normal rabbits was found by Grant and Gates [185] to cause an hypertrophy of the parathyroids. Nonidez and Goodale [186] found that when young chicks were kept on a ration poor in vitamin C and deprived of direct sunlight, an enlargement of the parathyroid gland resulted. It was due to an increase in the size and number of epithelial cells. This was followed by a phase of regression and in some cases by local degenerative changes. Subsequent exposure to sunlight led to a decrease of the gland volume with a considerable crowding of the epithelial cells and sometimes to pressure atrophy.

The irradiation of parathyroidectomized dogs did not significantly increase their blood calcium level, according to Swingle and Rhinhold.[187] Jung [188] however, found daily doses of ultraviolet light fifty times those commonly applied to unhabituated human subjects, to benefit parathyroidectomized white rats. He believed the parathyroid to have some function related to the photochemistry of the skin. Drucker and Faber [189] found that irradiation during tetany brought the calcium to a normal level without changing the blood pH or affecting the antagonistic relation between phosphorus and calcium. The increase in total serum calcium does not occur immediately following the irradiation of children with tetany as is the case with inorganic phosphorus. Indeed, it comes subsequent to the effects on the tetany. Calcium in the ultrafiltrate is generally below 50 per cent of the total calcium before irradiation. It increases in successive determinations and comes to exceed 60 per cent of the total calcium. Later a gradual increase in total calcium ensues.[190]

Although Malczynski [191] found a considerable increase in the blood cholesterol of irradiated human subjects, Ornstein found no significant changes.[192] Pincussen and Zuckerstein [193] found the serum cholesterol unchanged in irradiated animals, although the total ether extract of the serum was definitely increased. In rabbits, Kultjugin [194] found irradiation to increase the cholesterol not over 30 per cent, although the blood fat was greatly increased after the second exposure.

Hubert [195] believes that patients with carcinoma usually show a decrease in the serum cholesterol after irradiation. There are, however, so many exceptions that it is unlikely that this response to irradiation can have diagnostic significance.

[183] Moritz, A. R., *J. Biol. Chem.*, **64**, 81 (1925).

[184] Dell Aquila, A., and Jaia, F., *Arch. farmacol. sper.*, **60**, 578 (1935); *Chem. Abs.*, **30**, 4520 (1936).

[185] Grant, J. H. B., and Gates, F. L., *Proc. Soc. Exptl. Biol. Med.*, **21**, 230 (1924); *J. Exptl. Med.*, **45**, 115 (1927).

[186] Nonidez, J. F., and Goodale, H. D., *Am. J. Anatomy*, **38**, 319 (1927); *Chem. Abs.*, **21**, 2016 (1927).

[187] Swingle, W. W., and Rhinhold, J. S., *Am. J. Physiol.*, **75**, 59 (1925).

[188] Jung, F. T., *Endocrinology*, **12**, 81 (1928); *Chem. Abs.*, **22**, 2575 (1928); see also Vines, H., *Endocrinology*, **11**, 125 (1927); *Chem. Abs.*, **21**, 3960 (1927).

[189] Drucker, P., and Faber, F., *J. Biol. Chem.*, **68**, 57 (1926).

[190] Careddu, G., *Atti soc. med. Padova*, **15**, 126 (1937); *Chem. Abs.*, **32**, 6273 (1938).

[191] Malczynski, S., *Compt. rend. soc. biol.*, **99**, 922 (1928); *Chem. Abs.*, **23**, 401 (1929).

[192] Ornstein, T., *Compt. rend. soc. biol.*, **103**, 190 (1930); *Chem. Abs.*, **25**, 117 (1931).

[193] Pincussen, L., and Zuckerstein, E., *Biochem. Z.*, **207**, 426 (1929).

[194] Kultjugin, A., *Biochem. Z.*, **186**, 36 (1927).

[195] Hubert, R., *Arch. Gynäkol.*, **146**, 51 (1931); *Chem. Abs.*, **25**, 5926 (1931); *Arch. Gynäkol.*, **149**, 433 (1932); **151**, 681 (1932); *Chem. Abs.*, **27**, 2462 (1933).

The total blood sulfur is said to be lowered after ten minutes of irradiation.[196] Free sulfur and oxidized sulfur diminished in a parallel manner, but the former much more rapidly than the latter, so that the ratio of oxidized sulfur to total sulfur was, in general, increased.[197]

In vitro irradiation of human blood serum lowers its surface tension, although the results of *in vivo* irradiation are uncertain.[198] The index of refraction of normal horse serum at 20°C. increased progressively from 1.3466 to 1.3531 during thirty minutes of irradiation. Beef plasma showed a similar behavior and there were similar increases in antitetanic, antistreptococcic and antidiphtheric sera.[199] The change is attributed to an alteration of the state of the proteins.

The gelatinization of serum is said to be accelerated by ultraviolet rays.[200]

An acceleration of the rate of red cell sedimentation is produced over only a limited range of dosages, beyond which the rate tends to be retarded.[201]

The blood and skin of rabbits which have been irradiated over a period of three to six weeks is found by Engel [202] to contain a substance which induces cornification in castrated female mice. Its formation is not promoted by the simultaneous injection of cholesterol. Ultraviolet irradiation of castrated female rats and mice does not produce a positive Allen-Doisy test.

Blood Enzymes. Pincussen [203] found the activity of the blood catalase of rabbits kept in darkness slightly greater than that of animals exposed to ultraviolet light, especially if they had been given a sensitizer. In rats, the diminution is especially marked in the liver.[204] Koldayev and Altschuller [205] noted a transitory decrease in the serum amylase and blood catalase of irradiated rabbits. Castagna [206] found the longer rays of sunlight to increase the blood catalase of mice over that in those kept in darkness, these having almost none. Irradiation in the wavelength range 3190 to 3900A did not materially change the catalase content. When both this radiation and visible light were used, the catalase content increased during the first three hours of irradiation and then declined. Daily sunbaths are said to cause a small increase in human blood catalase.[207]

The general irradiation of rabbits produces a proteinase capable of attacking skin and serum proteins, according to Abderhalden and Tetzner.[208] Schamberg and Brown [209] find that exposure of rabbits to ultraviolet light decreases the concentration of lipase and increases that of proteinase in the blood. In the skin, both are decreased. Vedder [210] observed that when leucocytes are irradiated with visible light, the granules which contain oxidase disappear only if the temperature is raised above 62°. Ultraviolet irradiation, however, is effective at ordinary temperatures.

[196] Loeper, M., Degos, R., and Lesure, A., *Compt. rend. soc. biol.*, **106,** 718 (1931); *Chem. Abs.*, **25,** 3370 (1931).
[197] See also Loeper, M., Decourt, J., Olivier, J., Tonnet, J., and Lesure, A., *Compt. rend. soc. biol.*, (1926-7).
[198] Gobel, *Biochem. Z.*, **190,** 95 (1927); Tamura, A., *Acta Schol. Med. Univ. Kyoto,* **16,** 253 (1934); *Chem. Abs.*, **28,** 4754 (1934).
[199] Cluzet, J., and Kofman, T., *Compt. rend. soc. biol.*, **98,** 978 (1928); *Chem. Abs.*, **22,** 3179 (1928).
[200] Kopaczewski, W., *Compt. rend.*, **198,** 1947 (1934).
[201] Kostyal, L., *Biochem. Z.*, **299,** 100 (1930).
[202] Engel, P., *Endokrinologie,* **20,** 86 (1938); *Chem. Abs.*, **32,** 8452 (1938).
[203] Pincussen, L., *Biochem. Z.*, **168,** 474 (1926).
[204] Pincussen, L., and Tanino, F., *Biochem Z.*, **234,** 478 (1931).
[205] Koldayev, B., and Altschuller, M. M., *Z. physiol. Chem.*, **186,** 223 (1930).
[206] Castagna, S., *Biochim. terap. sper.*, **13,** 48 (1926); *Chem. Abs.*, **20,** 2529 (1926); *Arch. sci. biol. ital.*, **10,** 118 (1927); *Chem. Abs.*, **22,** 97 (1928).
[207] Deribas, D., and Kornmann, J., *Bull. soc. chim. biol.*, **18,** 418 (1936); *Chem. Abs.*, **30,** 5244 (1936).
[208] Abderhalden, E., and Tetzner, E., *Fermentforschung,* **14,** 522 (1935); *Chem. Abs.*, **29,** 8010 (1935).
[209] Schamberg, J. F., and Brown, H., *Arch. Int. Med.*, **35,** 537 (1925).
[210] Vedder, A., *Nederland. Tijdschr. Geneeskunde,* **68,** 2357 (1924); *Chem. Abs.*, **19,** 1143 (1924).

Effects on Immune Bodies in Blood. In general, irradiation does not affect the bactericidal properties of the blood of an irradiated subject.[211] After long periods of intense ultraviolet irradiation of rabbits, Albela [212] found no alteration of the phagocytic action of the blood serum, as determined by the concentration of opsonins. Koopman [213] observed that although the complement of the blood of a guinea pig was almost doubled during the first hour of irradiation of the animal, its concentration decreased markedly during a further two hours of exposure. This usually produced death and the blood was found free from complement. Gordon and Wormall [214] did not find the irradiation of guinea pigs to increase the serum complement. Osborn [215] found an occasional increase in the case of young, weaned rats, but this could not be uniformly obtained. Mesik reports a sharp drop during the irradiation, with a return to normal upon its cessation.[216]

Matushita [217] found irradiation of the skin of rabbits with ultraviolet rays to increase the amount of antityphoid substance in the serum (confirmed by Mesik), an effect especially marked in the serum of immunized animals. Both the skin and the spleen were necessary for irradiation to evoke this response. Irradiation of the skin was believed to produce a histamine-like substance which causes the spleen to release a hormone that controls the production of the antityphoid substance. Bessemans and Seldeslacht [218] found that rabbits injected with an emulsion of typhoid bacilli and then treated with ultraviolet rays showed a larger production of antibodies than non-irradiated animals.

Heuer and Potthoff [219] found that an exposure of animals to ultraviolet rays had only a slight influence on the formation of antibodies. Pigmented animals show this influence more than unpigmented ones. However, at the height of antibody formation, when the titer is somewhat constant, exposure of animals to ultraviolet rays causes a very great increase in the titer. This effect is not permanent and the return of the titer to the preimmunization level is much more rapid than in nonexposed animals. Wenger [220] finds carbon-arc irradiation of a small area on the back of a pig sufficient to produce a slight erythema to cause a moderate increase in the bactericidal action of the blood. This effect is considerable, he believes, when the erythema is severe.

Abe finds that irradiation of black rabbits accelerates the production of the agglutinin for *B. coli,* more marked than in white rabbits. [221]

The antitryptic activity of rabbit serum is said to increase after ultraviolet irradiation.[222]

Giaume [223] claimed that irradiated normal horse serum does not produce anaphylactic shock in sensitized guinea pigs. Five minutes of irradiation of the sensitized

[211] Tataranu, F., *Compt. rend. soc. biol.*, **97,** 1736 (1927); *Chem. Abs.*, **22,** 1799 (1928).
[212] Albela, D., *Deut. med. Wochschr.*, **48,** 1347 (1922); *Chem. Abs.*, **17,** 140 (1923).
[213] Koopman, J., *Deut. med. Wochschr.*, **50,** 277 (1924); *Chem. Abs.*, **18,** 2197 (1924).
[214] Gordon, J., and Wormall, A., *Biochem. J.*, **22,** 909 (1928).
[215] Osborn, T. W. B., *Biochem. J.*, **25,** 2136 (1931).
[216] Mesik, R. E., *Arch. sci. biol. (U.S.S.R.),* **40,** 31 (1936); *Chem. Abs.*, **31,** 6726 (1937).
[217] Matushita, M., *J. Chosen Med. Assoc.*, **22,** 787 (1932); *Chem. Abs.* **27,** 2208 (1933).
[218] Bessemans, A., and Seldeslacht, A., *Compt. rend. soc. biol.*, **99,** 628 (1928); *Chem. Abs.*, **23,** 435 (1929).
[219] Heuer, G., and Potthoff, P., *Centralbl. Parasitenk.*, **I, 88,** 299 (1922); *Chem. Abs.*, **17,** 144 (1923).
[220] Wenger, W. J., *Z. Immunitäts* **93,** 501 (1938); *Chem. Abs.*, **32,** 9248 (1938).
[221] Abe, G., *Sei-i-kai Med. J.*, **56,** No. 11, 2169 (1937); *Chem. Abs.*, **32,** 5438 (1938).
[222] Yamanaka, G., Sei-i-kwai; *Med. J.*, **48,** 3, 62 (1929); *Chem. Abs.*, **23,** 4263 (1929).
[223] Giaume, C., *Pediatria Rivista,* **35,** 1111 (1927); *Pathologica,* **20,** 236 (1928); *Chem. Abs.*, **22,** 2202 (1928).

animal lessens the shock produced by normal serum. Severe and even fatal shocks result when both the sensitizing agent and the shock-producing material have been irradiated. Brotzu [224] finds daylight or light in the range 5100 to 7700A to be more effective than blue-violet light or darkness in aiding the production of agglutinins in guinea pigs injected with the Gaertner bacillus or with the cholera vibrio. Infrared rays stimulated more agglutinin formation than daylight, and ultraviolet rays more than blue-violet light. Guinea pigs exposed to infrared rays produce more bacteriolysins than those exposed to ultraviolet light.

Exposure of guinea pigs to red, yellow or blue light has no effect on the formation of anti-sheep hemolysins.[225]

It has been said that serums obtained from rabbits inoculated with organisms grown on ultraviolet-irradiated agar show greater agglutinating, bacteriolytic and complement materials than those in the production of which the organisms had been grown on ordinary agar.[226]

There have been several recent investigations of the effect of ultraviolet light upon antigens. Intensive irradiation of horse serum for twenty to forty minutes destroys its ability to cause the characteristic anaphylactic contraction of the isolated uterus of guinea pigs sensitized to horse serum. The treated serum retains its ability to desensitize the uterus and after exposure to the treated serum, the uterine horns will no longer react with fresh, untreated serum. This densitization, however, requires a longer period than that produced by untreated actively shocking serum.[227] Different results were reported by Kitamura and Murayama [228] who found 0.1 cc. of thirty minute-irradiated horse serum or egg-white to produce the usual contraction of the uterus of sensitized guinea pigs. After washing and the lapse of twenty minutes, the addition of 0.5 cc. of normal serum also produced a contraction, indicating that desensitization had not been attained. Then, after ten minutes, the addition of neither serum produced contraction.

The agglutinogens of red blood cells, which are said not to contain protein, are not affected by ultraviolet light.[229]

Heuer [230] reported that antibodies are sensitive to ultraviolet rays when diluted. The agglutinins for cholera and paratyphoid A were believed less resistant to ultraviolet rays than those for typhoid, although this was controverted by Ninomiya.[231] Heuer believed the bateriolysins less resistant than the agglutinins. Brawn [232] found ultraviolet light to destroy complement but to have no effect on cholesterolized antigen or on Wassermann negative or positive human serums. Gordon and Wormall [233] found that the destruction of serum complement is not due to oxidation, although the rate of inactivation appeared to be slightly less in a vacuum than in air. It is the heat-labile protein component that is most affected. Levine [234] attributes the destruction to the coagulation of certain protein components.

[224] Brotzu, G., *Boll. soc. ital. biol. sper.*, **8**, 1722 (1933); *Chem. Abs.*, **28**, 4470 (1934).

[225] Diacono, H., *Arch. Inst. Pasteur Tunis*, **20**, 48 (1931); *Chem. Abs.*, **25**, 4312 (1931).

[226] Marras, F. M., and Omar, W., *J. Egyptian Med. Assoc.*, **17**, 687 (1934); *Chem. Abs.*, **28**, 7288 (1934).

[227] Kallós, P., and Kallós-Deffner, L., *Klin. Wochschr.*, **14**, 392 (1935); *Chem. Abs.*, **30**, 3058 (1936).

[228] Kitamura, S., and Murayama, M., *Klin. Wochschr.*, **16**, 88 (1937); *Chem. Abs.*, **31**, 3555 (1937).

[229] Dujarric de la Rivière, R., and Kossovitch, N., *Ann. inst. Pasteur*, **55**, 331 (1935); *Chem. Abs.*, **30**, 4206 (1936).

[230] Heuer, G., *Centralbl. Bakt. Parasitenk.*, **I, 88**, 380 (1922).

[231] Ninomiya, R., *Z. Immunitäts.*, **39**, 494 (1924); *Chem. Abs.*, **18**, 2555 (1924).

[232] Brawn, G., *Z. Immunitäts.*, **44**, 27 (1925); *Chem. Abs.*, **20**, 1267 (1926). See also Bovie, W. T., *J. Med. Research*, **38**, 335 (1918).

[233] Gordon, J., and Wormall, A., *Biochem. J.*, **22**, 909 (1928).

[234] Levine, B. S., *Am. Med.*, **35**, 610 (1929); *Chem. Abs.*, **24**, 2174 (1930). See also Friedberger, E., and Scimone, V., *Z. Immunitäts.*, **37**, 341 (1923); *Chem. Abs.*, **18**, 551 (1924).

Hassko [235] states that complement, the antibodies in positive human serums, amboceptors, agglutinins and precipitins all lose their specific activity partly or completely under the influence of ultraviolet rays, the extent depending upon the dilution of the protein, its colloidal properties and various other conditions. Egg albumin irradiated for nine hours is non-precipitable by neoarsphenamine. Paic and Haber [236] find the inhibiting action of mixed light on complement to be appreciable after thirty minutes of irradiation. Destruction is complete after ten hours. Petterson [237] maintains that ultraviolet rays are more active than visible light in inactivating *in vitro* the bactericidal substances of the body. Serum alexin is much more sensitive than β-lysin and the bactericidal substances of white blood cells. Active β-lysin is as sensitive as the inactivated substance. Blanchard [238] finds the opsonic activity of normal cat serum decreased on exposure to a mercury-arc lamp. He suggests that irradiation inactivates the opsonins, which are probably protein-like, by changing their colloidal state.

Growth. Studies have been made of the effect of daily irradiations of animals upon their growth. Leigh-Clare [239] found that, if their eyes were shielded, exposures of young growing rats for periods up to thirty minutes daily had no deleterious effect. Suzuki and Hatano [240] concluded from a series of experiments with white rats, chickens and rabbits, that the ultraviolet rays present in ordinary daylight are far from sufficient for the vigorous development of young chicks.

The rate of growth or the histological anatomy of the thyroid gland of rats is unaffected by daylight, darkness or ultraviolet light environments during their growth, according to Mayerson.[241]

Tadpoles receiving dried milk from thyroidectomized, nonirradiated goats were found by Kucera and Soos [242] to grow slowly and develop abnormally small thyroids. If the udder of the thyroidectomized goat was irradiated, the retarding effect of the milk on the tadpoles was decreased, but they did not develop as fast as those receiving milk from normal goats. The milk from irradiated thyroidectomized goats receiving potassium iodide permitted more rapid development. Rats kept in darkness have an average blood iodine of 25 γ per cent. In the dried thyroid gland there is 211 γ per cent.[243] The gland has the histological picture of increased activity, that is, less colloid, an increased number of follicles and high irregular epithelial cells. Rats given Vigantol or ultraviolet irradiation have a high blood iodine (30 to 40 γ per cent), a low thyroid iodine content (112-167 γ per cent) and the histologic picture of increased colloid and flat, resting epithelium.[244]

Effects on the Secretory Activity of Glands. Doses of ultraviolet light strong enough to cause a rapid erythema exert a histamine-like effect upon gastric secretions, causing the appearance of free hydrochloric acid in patients with so-called histamine achylia, according to Diehl.[245] Sunbaths are also said to stimu-

[235] Hassko, S., *Biochem. Z.*, **226**, 462 (1930).

[236] Paic, M., and Haber, P., *Compt. rend.*, **198**, 613 (1934).

[237] Petterson, A., *Z. Immunitäts.*, **75**, 156 (1932); *Chem. Abs.*, **26**, 5646 (1932).

[238] Blanchard, E. W., *Physiol. Zoöl.*, **4**, 316 (1931); *Chem. Abs.*, **25**, 4599 (1931).

[239] Leigh-Clare, J. L., *Biochem. J.*, **21**, 208 (1927).

[240] Suzuki, K., and Hatano, T., *Bull. Agr. Chem. Soc. Japan*, **3**, 14; *Chem. Abs.*, **22**, 1182 (1928).

[241] Mayerson, H. S., *Am. J. Physiol.*, **113**, 659 (1935). See, however, Bennholdt-Thomsen and Ziegler-Wellmann.[243]

[242] Kucera, C., and Soos, M., *Compt. rend. soc. biol.*, **113**, 619 (1933); Andrik, L., and Kucera, C., *Ibid.*, 622; *Chem. Abs.*, **27**, 4564 (1933).

[243] Bennholdt-Thomsen, C., and Ziegler-Wellmann, M., *Klin. Wochschr.*, **13**, 800 (1934); *Chem. Abs.*, **28**, 6734 (1934).

[244] For the effect of ultraviolet rays on lymphoid tissue, see Jolly, J., *Compt. rend. soc. biol.*, **93**, 999 (1925).

[245] Diehl, F., *Arch. exptl. Path. Pharmakol.*, **159**, 367 (1931).

late gastric secretion.[246] The usual daily variations in the acidity of the gastric juice are, however, so great as to make definite conclusions somewhat uncertain.[247] Considerable decreases in the secretory activity of the pancreas occur from three to five hours after fifteen to thirty minutes of irradiation of dogs.[248] With shorter irradiation periods (seven minutes) the effects were variable. The effect is attributed to a substance brought to the gland by the blood and produced originally by the irradiation.

Gedda [249] finds a fifteen-minute irradiation of human subjects to have a diuretic effect, increasing not only the volume of urine but also its content of urea and especially of chlorides.

Light treatment particularly by visible rays, increases the accumulation of zinc [250] in the tissues of animals to which the metal is administered over that of animals receiving the same amount but not irradiated. Pincussen has discussed [251] the acceleration of the excretion of lead brought about by irradiation. Pincussen and Roman[252] demonstrated that irradiation by the mercury arc increases the ratio of organic to inorganic iodine in both normal and dye-injected mice. It also increases the organic bromine at the expense of the inorganic bromine but has no similar effect upon the distribution of chlorine.

A number of experiments have been made upon portions of non-intact animals. Azuma and Hill [253] found irradiation of involuntary muscle by ultraviolet rays antagonized the action of adrenalin but not that of emetine. These rays increase the tone and rhythmic contractions of the muscle of the frog rectum if there is calcium in the nutrient fluid employed.[254] In the presence of magnesium, however, they cause relaxation and cessation of rhythmic contractions. The presence of calcium ions is also necessary for ultraviolet rays to stimulate the contraction of skeletal muscle suspended in Tyrode's solution. Potassium and magnesium ions appeared to moderate the effect of the calcium ions.[255]

Petersson [256] believes ultraviolet light weakens the parasympathetic excitability of the surviving intestine and uterus by diminishing the excitability of the sympathetic inhibitor and increasing that of the sympathetic motor. These modifications of excitability are thought to be durable and to persist after the cessation of the irradiation.

Ultraviolet light directly stimulates the contracture of skeletal muscle of the frog independently of the presence of molecular oxygen.[257] The redox potential is increased, the maximum effect being produced by ten minutes of irradiation.[258] Larger doses inhibit the change. The effect is produced immediately after the exposure to ultraviolet rays. For the effect to occur, the dehydrogenase and hydrogen donor system must be present. At an optimum dosage, the reduced glutathione increases, the reverse occurring when excessive doses are used. Ashkenaz finds stimulation by ultraviolet light causes muscle fibers to give off calcium.[259]

It has been shown by Kler [260] that under suitable conditions, ultraviolet rays stimulate a rhythmic contraction of the heart *in vitro*. The cardiac effects of atropine are also influenced by irradiation of a human subject to whom it is administered, according to

[246] Barone, V. G., *Arch. Fisiol.*, **31**, 468 (1932); *Chem. Abs.*, **27**, 1667 (1933).
[247] Keller, P., and Loeb, M., *Klin. Wochschr.*, **4**, 2390 (1925); *Chem. Abs.*, **20**, 922 (1926).
[248] Glikson, E. B., *Arch. sci. biol. (U.S.S.R.)*, **39**, 629 (1935); *Chem. Abs.*, **30**, 6023 (1936).
[249] Gedda, L., *Minerva Med.*, **I**, 841 (1933); *Chem. Abs.*, **27**, 4300 (1933).
[250] Nakadate, K., *Biochem. Z.*, **265**, 61 (1933).
[251] Pincussen, L., *Klin. Wochschr.*, **12**, 275 (1933).
[252] Pincussen, L., and Roman, W., *Biochem. Z.*, **216**, 3336 (1929).
[253] Azuma, Y., and Hill, L., *Proc. Roy. Soc.*, **99B**, 221 (1926).
[254] Azuma, Y., *Proc. Roy. Soc.*, **100B**, 431 (1926).
[255] Azuma, Y., *Proc. Roy. Soc.*, **101B**, 24 (1927).
[256] Petersson, F., *Compt. rend. soc. biol.*, **99**, 1677 (1928); *Chem. Abs.*, **23**, 622 (1929).
[257] Spealman, C. R., and Blum, H. F., *J. Cellular Comp. Physiol.*, **3**, 397 (1933).
[258] Uchimura, T., *J. Biochem. (Japan)*, **25**, 207 (1937); *Chem. Abs.*, **31**, 5395 (1937).
[259] Ashkenaz, E. W., *J. Cellular Comp. Physiol.*, **12**, 139 (1938); *Chem. Abs.*, **32**, 9112 (1938).
[260] Kler, S., *Compt. rend. soc. biol.*, **93**, 1391 (1925); *Chem. Abs.*, **20**, 1821 (1926); see also Wastl, H., *Arch. exptl. Path. Pharmakol.*, **114**, 56 (1926).

Garot.[261] When administered immediately after the irradiation of children it causes an acceleration of the pulse rate more rapidly but less marked than in the case of non-irradiated subjects.

A substance present in alcoholic extracts of skeletal muscle which stimulates the action of the isolated toad heart is not affected by irradiation, according to Oana.[262] Haberlandt [263] believes the stimulating substance which may be extracted from the heart of the frog in Ringer's solution can be partly, but not completely, destroyed by ultraviolet light. In this respect he thought it to resemble adrenaline and the accelerating substance of Loewi.

Offant and Dubouloz [264] claimed that the rhythm of the perfused frog heart can be affected by the use of irradiated Ringer's solution as the perfusion fluid, unless the solution had been kept at 100° during irradiation. Renosto,[265] however, found that, in the absence of sensitizers, ultraviolet irradiation of either the heart itself or the perfusion fluid had no effect. In the presence of dyestuffs in the perfusion liquid there could be observed, after a latent period following irradiation, a lessened amplitude of the contractions of the heart without any change in the tone, rhythm or frequency.

Recently, Guttman [266] found that after the rhythm of frog or Limulus hearts had been stopped by the addition of an excess of potassium to the perfusion fluid, it could be promptly restored by ultraviolet irradiation. He also noted [267] that irradiation of the clam heart in sea water for two or three minutes caused a marked increase in tonus and a definite decrease in amplitude, but that the pace-maker was not affected. It was suggested that irradiation may increase the permeability of the cells, permitting potassium to leave and calcium to enter. The rate of the Limulus heart in sea water was increased by ultraviolet irradiation. The same effect was observed when the heart was shielded from the rays and masses of skeletal or smooth muscle were irradiated instead. This was explained by the assumption of the production of an accelerator substance in these tissues which diffuses to the heart. About twenty minutes after the cessation of the irradiation, the frequency and amplitude are diminished, possibly because of the formation of a depressor substance.[268]

Milk. In women, ultraviolet irradiation appeared to increase the quantity of milk secreted in ten of fifteen cases studied by Lesné and Dreyfus-Sée.[269] Aside from an increase in the antirachitic properties of the milk, its chemical composition was unaffected. Knott and Garver [270] found that irradiation of the udders of cows for twenty minutes daily for 21 days had no significant effect upon the quantity of milk produced or on the content of its butter fat or total solids.

Martini [271] finds the milk of various species of animals to exhibit different powers of reducing methylene blue in light. The most active is that of sheep. Cows' milk loses this power very easily, especially if exposed to light. The property is ascribed, not to the fatty components of the milk, but rather to a thermostable, water-soluble substance, possibly glutathione.

The oxidation-reduction potentials of cream and whole or skimmed milk drift toward the negative side on exposure to light.[272] This potential change is accentuated by the addition of methylene blue. As the solutions develop a progressively more negative potential, methylene blue becomes decolorized when this potential

[261] Garot, L., *Compt. rend. soc. biol.*, **96**, 1048 (1927); *Chem. Abs.*, **21**, 2333 (1927).
[262] Oana, M., *Japan. J. Exptl. Med.*, **10**, 123 (1932); *Chem. Abs.*, **26**, 4852 (1932).
[263] Haberlandt, L., *Arch. ges. Physiol., (Pflüger's)*, **218**, 129 (1927); *Klin. Wochschr.*, **6**, 2099 (1927).
[264] Offant, C., and Dubouloz, P., *Compt. rend. soc. biol.*, **112**, 373 (1933); **115**, 1300 (1934); *Chem. Abs.*, **28**, 4479 (1934).
[265] Renosto, G., *Boll. soc. ital. biol. sper.*, **10**, 295 (1935); *Chem. Abs.*, **29**, 6308 (1935).
[266] Guttman, S. A., *J. Cellular Comparative Physiol.*, **8**, 37 (1936); *Chem. Abs.*, **30**, 5662 (1936).
[267] Guttman, S. A., *Proc. Soc. Exptl. Biol. Med.*, **33**, 363 (1935); *Chem. Abs.*, **30**, 8250 (1936).
[268] Guttman, S. A., *Biol. Bull.*, **72**, 75 (1937).
[269] Lesné, E., and Drefus-Sée, G., *Lait*, **11**, 155 (1931); *Chem. Abs.*, **25**, 4032 (1931).
[270] Knott, J. C., and Garver, H. L., *Ann. Report Washington Agr. Expt. Sta., Bull.* **260**, 27 (1931); *Chem. Abs.*, **26**, 4615 (1932).
[271] Martini, V., *Boll. soc. ital. biol. sper.*, **6**, 773 (1931); *Chem. Abs.*, **26**, 1631 (1932).
[272] Aikins, G. A., and Fay, A. C., *J. Agr. Research*, **44**, 85 (1932); *Chem. Abs.*, **26**, 3045 (1932); Martini, E., *Biochem. Z.*, **260**, 153 (1933).

reaches that capable of reducing the dye. Similarly, the blue color reappears when the solution develops a potential sufficiently positive to oxidize the dye. The addition of fat to skimmed milk hastens the reduction time of methylene blue in samples exposed to sunlight, probably because of the tendency of the fat to elevate the zone of reduction. However, the reducing intensity induced by the growth of bacteria is more negative than that induced by sunlight. This indicates that the photoreduction of methylene blue in milk is a reaction distinct from that produced by bacteria. When skimmed milk containing methylene blue decolorized by sunlight is placed in darkness, the potential quickly becomes sufficiently positive to oxidize the leuco-base. Artificial light hastens the reduction of methylene blue in market milk. Light from a 75-watt electric bulb produces a potential drift in milk which differs only in degree from that observed in sunlight. Similar observations that the oxidation of fat in whole milk under the influence of sunlight causes the development of a reducing potential detected by its effect upon methylene blue or electrometrically were made by Whitehead.[273]

Effects of Ultraviolet Light Upon the Eye Media

As the sense-organ of reception of solar radiations, the retina would seem to require especial protection. It is, therefore, not surprising that the structures of the eye through which the rays must pass in order to reach the retina act as filters of potentially injurious rays. Against natural ultraviolet the cornea affords little protection, as it is transparent to rays of wave-length greater than 2950A.[274] The vitreous and aqueous humors transmit the ultraviolet down to 3000A, according to Birch-Hirschfeld.[275] It is the lens of the eye which is chiefly responsible for stopping ultraviolet rays from reaching the retina.

de Chardonnet [276] used a quartz plate coated with a silver film of such a thickness as to be opaque to the visible and invisible spectrum except for the region between 3010 and 3430A. Through this plate normal eyes could not see an arc light, but eyes from which the lens had been removed in the operation for cataract could detect the movements of the arc.

In addition to its absorptive power, the lens can alter the rays by fluorescence. The fluorescence is excited by rays between 3500 and 4000A. Thus we see that no radiation of wave-length shorter than 3500 (or more probably 3800A) can reach the retina. In the later period of life, owing to yellowing of the media, the limit is pushed into the most refrangible region of the visible spectrum. Opinions differ greatly as to the limit of visibility. Some claim to have seen the line in the tin spectrum at 3175A.[277] This may possibly have been due to stray reflections in the monochromators employed. Saidman and Dufestel [278] claim to have seen faintly a line at 3650A.[279]

Exposure of the eyes to ultraviolet rays results in inflammation, but only of the superficial structures. This effect, which has been described in Chapter 10, is

[273] Whitehead, H. R., *Biochem. J.*, **25**, 1647 (1931).

[274] Martin, E. K., *Proc. Roy. Soc.*, **85**, 319 (1912); Schanz, F., and Stockhausen, K., *Arch. für Ophth.*, **69**, 49 (1908).

[275] Birch-Hirschfeld, A., *Arch. für Ophth.*, **71**, 573 (1909).

[276] de Chardonnet, *Compt. rend.*, **96**, 509 (1883).

[277] Glancy, A. E., *Am. J. Physiol. Optics*, **4**, 145 (1923); Graham, W. P., *J. Opt. Soc. Am.*, **6**, 605 (1922).

[278] Saidman, J., and Dufestel, L. G., *Compt. rend.*, **182**, 1173 (1926).

[279] For a very detailed study of the transmission of the various media of the eye and of the eye as a whole, see Shoji, Y., *Mitt. Med. Fak. Univ. Tokoyo*, **29**, 61 (1922). This is discussed in Laurens, H., "The Physiological Effects of Radiant Energy," p. 150. New York, The Chemical Catalog Co., Inc., (Reinhold Publishing Corp.), 1933.

strictly comparable with the inflammations of the skin which are intentionally provoked as part of the routine of ultraviolet therapy. Like these, the conjunctival inflammation subsides rapidly without leaving any trace. It is rarely desirable to produce such a reaction. Verhoeff and Bell,[280] who made elaborate studies of the reaction, conclude that conjunctivitis is caused by rays of wave-lengths shorter than 3050A.

Many studies have been made upon the lens, particularly because of the possibility of a relation to the ultraviolet rays of sunlight and the production of cataracts. Burge [281] concluded that ultraviolet rays can change cell protoplasm in such a manner that certain salts may combine with it to form a precipitate or coagulum. Abnormal amounts of sodium silicate or calcium salts in the cells of the eyelids or the cornea augment the inflammatory action of the radiations. By exposing fish, living in dilute solutions of certain salts, to ultraviolet rays, he was able to produce cataracts.

The observations of Schanz [282] on the lens have shown that the effect of light is to render its proteins less soluble. The frequency of lenticular opacity in diabetes suggested a series of experiments in which equal amounts of a protein solution in each of a series of quartz test tubes were irradiated in the presence of increasing amounts of acetone. The results showed that the loss of solubility of the protein is increased by the presence of acetone.

Adams [283] finds that, although in patients with senile cataracts the serum calcium is appreciably higher than normal, calcium salts acting on fresh ox lenses do not cause opacity unless present in non-physiological concentrations. Nor could she find them to act as sensitizers to ultraviolet radiations as had been suggested by Burge.

All wave-lengths, including infrared, visible and ultraviolet, are said by Burge, Wickwire and Schamp [284] to be capable of rendering the lens material electronegative and so being effective in producing its calcification. It is difficult to explain this behavior of the longer wave-lengths physically and these authors note the shorter wave-lengths to be much the more effective. Hinrichs [285] suggests that the effect of ultraviolet irradiation of excised lenses in 0.1- to 1-per cent solutions of sodium chloride and calcium chloride is probably a surface phenomenon. There is involved a change in the permeability to salts or their ions and a subsequent precipitation of the lens protein. Calcium is more effective than sodium in producing the lens opacity.

Opinion at present does not ascribe the origin of cataracts in glass workers to visible rays and probably not to the direct action of either the infrared rays or the ultraviolet rays. Bradford and others suggested [286] the possibility that an indirect action on the nutrition of the lens may be ascribed to the action of the infrared rays on the iris and ciliary bodies.[287]

Lieben and Kronfeld [288] illuminated the lenses of fresh intact pigs' eyes with diffused daylight in the presence of a sensitizer and also by a quartz lamp both

[280] Verhoeff, F. H., and Bell, L., *Proc. Am. Acad. Arts Sci.*, **51**, 640 (1916).

[281] Burge, W. E., *Am. J. Physiol.*, **39**, 335 (1916).

[282] Schanz, F., *Arch. ges. Physiol. (Pflüger's)*, **170**, 646 (1918); *J. Chem. Soc.*, **118**, II, 213 (1920).

[283] Adams, D. R., *Biochem. J.*, **23**, 902 (1928).

[284] Burge, W. E., Wickwire, G. C., and Schamp, H. M., *Arch. Ophthalmol.*, **17**, 234 (1937); *Chem. Abs.*, **31**, 3133 (1937).

[285] Hinrichs, M., *Proc. Soc. Exptl. Biol. Med.*, **27**, 535 (1930).

[286] Report of Glass Workers' Cataract Committee, *Proc. Roy. Soc.*, **103B**, 192 (1928).

[287] Note also Sheard, C., *Am. J. Physiol. Optics*, **5**, 214 (1924).

[288] Lieben, F., and Kronfeld, P., *Biochem. Z.*, **197**, 136 (1928).

with and without a sensitizer. In no case could there be observed any decrease in the tryptophane content of the lens proteins. Under the same conditions in solutions of the lenses in alkali, containing the equivalent of 0.5 per cent of protein, considerable destruction of this amino- acid occurred, but since the destruction did not occur in solutions four times as concentrated, it was assumed that the protein of the lens is protected in high concentrations from chemical changes due to light. Normal human lenses and those with cataracts showed no difference in the tryptophane content of their protein.

The ability of the lens to oxidize certain organic acids (fumaric, malic and succinic) is decreased by exposure to ultraviolet light.[289]

The glutathione content of the ox lens is decreased by exposure to ultraviolet light and to a more marked extent by heat rays. Frog eyes not exposed to light show an oxygen consumption of the order of 6.5 cu. mm. per gm. of tissue per minute. This is decreased by exposure to light.[290]

The lactic acid content of the aqueous humor is unaffected by keeping animals in light or darkness.[291] The natural vitreous humor of pH 8.2 absorbs near 2600 to 2700A, differing from the crystalline humor which absorbs at 2760A.[292]

Effects of Ultraviolet Light on Development of Simple Organisms

Lillie and Baskerville [293] in reporting experiments on starfish eggs, state the effects produced in unfertilized eggs by brief irradiation with ultraviolet rays to resemble those of partial activation. The immediate change produced in the egg system is of the same essential nature as that caused by temporary exposure to high temperature or other activating agent. The primary effect of the rays is probably a structural change, that is a change in the colloidal substratum of the protoplasm and probably of the surface layer, upon which follow specific chemical effects as a secondary consequence.

Exposure of the eggs of *Chaetopterus* for sixty to seventy seconds at 21.5 cm. from a mercury arc leads to a tendency of the eggs to fuse, after insemination, during the cleavage stages into masses of twelve to fifteen eggs, because of changes in the cortex.[294]

Irradiation of normal *Arbacia* eggs produces at first a slight increase, then a decrease and finally a complete loss of the power of producing fertilizin.[295] The irradiation of normal egg water produces a fading of the echinochrome pigment, a slight increase in the pH, and a reduction of the agglutination of fertilizin. The more concentrated suspensions of sperm show an increase of viscosity and a decrease of surface tension following irradiation. Irradiated sperms show a reduction of agglutinability by normal egg water. The more dilute suspensions are the more susceptible.

Vlès and Gex [296] found the principal absorption band of sea urchin eggs to be at about 2800A.

The growth of cultures of connective tissue may be inhibited by an eight

[289] Adams, D., *Proc. Roy. Soc.*, **98B**, 244 (1925); *Biochem. J.*, **23**, 902 (1929).
[290] Noyons, A., and Wiersma, C., *Acta Brevia Neerland. Physiol. Pharmacol. Microbiol.*, **3**, 156 (1933); *Chem. Abs.*, **28**, 7337 (1934).
[291] Wittgenstein, A., and Gaedertz, A., *Biochem. Z.*, **176**, 1 (1926).
[292] Abe, T., *Arch. phys. biol.*, **6**, 1 (1927); *Chem. Abs.*, **23**, 3499 (1929).
[293] Lillie, R. S., and Baskerville, M. L., *Am. J. Physiol.*, **61**, 57 (1922); *Chem. Abs.*, **16**, 2937 (1922); *cf.* Baldwin, W. M., *Biol. Bull.*, **37**, 294 (1919); *Chem. Abs.*, **14**, 1164 (1920).
[294] Just, E. E., *Science*, **71**, 72 (1930).
[295] Hinrichs, M. A., *Biol. Bull. Marine Biol. Lab.*, **53**, 416 (1927); *Chem. Abs.*, **22**, 463 (1928).
[296] Vlès, F., and Gex, M., *Bull. Inst. Oceanograph*, **658**, 23 pp. (1934); *Chem. Abs.*, **29**, 2184 (1935).

to ten minutes' exposure to ultraviolet rays, but the cells regain their proliferative power when transferred to a fresh medium. The lethal dose is ten to fifteen times as large.[297]

Chick embryos show a differential susceptibility to ultraviolet irradiation, the regions of greatest physiological activity being the most easily modified by sublethal doses.[298] These same regions also die and disintegrate the most rapidly on the application of lethal doses. In the embryonic stages there is a single anteroposterior gradient of susceptibility which in later stages is complicated by the appearance of local regions of high susceptibility. In general, the susceptibility to the modification of development by ultraviolet irradiation is proportional to the dosage.

The effects of local ultraviolet irradiation of developing embryos of *Triton taeniatus* are largely limited to the surface cells, according to Dürken,[299] probably on account of the great light absorption by the yolk granules. The result is a pigmentation of the irradiated area, followed by a contraction of the surface of the cell, which forces out its contents. In the later stages of development, irradiation kills the entire cell on which it falls, and the dead cell is either thrown out or, in still older embryos, remains within the organism without undergoing further development. Irradiation of the organizer region of the *Triton* embryo can completely or partially inhibit the organizing action without killing the embryo.[300] Since the active substance appears to be very stable, its direct inactivation by light seems improbable. Reith, however, regards the power of induction by the organizer region (blastopore lip) when implanted in normal gastrulae as very resistant to ultraviolet radiations.[301]

To determine the nature of the colloidal changes which occur in irradiated protoplasm, Remotti [302] bred some of the young of *Salmo lacustris* in darkness and exposed others to a 1000 c.p. electric light. The serum drawn from the irradiated and sectioned embryos reacted more slowly with hydroquinol than that from non-irradiated ones.

Chick embryo cells grown in media containing cancer-producing hydrocarbons are photosensitive. Methylcholanthrene, 1,2,5,6-dibenzanthrene and 1,2-benzopyrene in concentrations of 0.05 to 0.1 per cent do not affect the growth or mitosis of the cells until the cultures are exposed to a bright light. Exposures of two to ten minutes cause changes in the cells and inhibit mitosis, but the cells subsequently recover and proliferate, unless the exposures have been unduly prolonged.[303]

Ultraviolet irradiation of the larvae of *Drosophila melanogaster* does not prolong the larval stage as do x-rays. The immediate effects on carbon dioxide formation were, however, similar, according to Thompson.[304] Small doses of ultraviolet light hasten the development of mosquito larvae, but larger amounts, and also complete darkness, are harmful.[305]

The penetration of acetic acid into the living larvae of frogs occurs more slowly

[297] Kler, S., *Compt. rend. soc. biol.*, **93**, 1389 (1925); *Chem. Abs.*, **20**, 1821 (1926).
[298] Hinrichs, M. A., *J. Exptl. Zoöl.*, **47**, 309 (1927); *Chem. Abs.*, **22**, 994 (1928).
[299] Dürken, B., *Z. wiss. Zoöl.*, **144**, 123 (1933); *Chem. Abs.*, **28**, 534 (1934).
[300] Dürken, B., *Z. wiss. Zoöl.*, **147**, 295 (1935).
[301] Reith, F., *Z. wiss. Zoöl.*, **150**, 179 (1937); *Chem. Abs.*, **32**, 3490 (1938).
[302] Remotti, E., *Atti accad. Lincei*, **3**, 772 (1926); *Chem. Abs.*, **20**, 3196 (1926).
[303] Lewis, M. R., *Am. J. Cancer*, **25**, 305 (1935).
[304] Thompson, W. R., *J. Gen. Physiol.*, **18**, 869 (1935).
[305] Frost, F. M., Herms, W. B., and Hoskins, W., *J. Exptl. Zoöl.*, **73**, 461 (1936); *Chem. Abs.*, **30**, 8404 (1936).

in darkness than in light.[306] If the larvae are exposed to ordinary light, the illumination is followed by no after-effects, but if the quartz lamp is used, a definite influence on the permeability of the larvae remains. The irradiation of tadpoles causes accelerated development, but that of frog and toad spawn is without effect.[307]

Higgins and Sheard[308] stated in respect to the early larval development of *Rana pipiens* that the stimulative action of light is due to the region between 4000 and 2800A and that lethal effects are due to wave-lengths shorter than 2800A. Ultraviolet rays stimulate the exogenous growth of cells and of the organism as a whole. However, they inhibit subsequent exogenous metabolic processes and therefore interfere with growth and cause death.

Neoplasms. The excess of nuclein phosphorus in cancerous tissue over that in normal tissue observed by Enselme and Enselme[309] disappears after ultraviolet irradiation. On the other hand, lipid phosphorus increases in the irradiated tumor at the same time as the proportion of fat. Under the influence of irradiation, the tendency is for the nuclear constituents to be decreased and for the cancerous tissue to be transformed into fat.

Strong irradiation with ordinary incandescent lamps seemed to accelerate the development of papillomas and cancers in mice treated with tar by Vlès, de Coulon and Ugo.[310]

Lecithin, especially after irradiation with ultraviolet light for 24 to 600 hours is said by Roffo[311] to inhibit the growth of sarcoma cells *in vitro*.

Roffo and Pilar[312] called attention to a possible relation between the increased cholesterol content of skin irradiated by ultraviolet light and the formation of tumors. They observed that 92 per cent of the skin tumors of the face occurred on the parts directly exposed to the sun. Keratotic carcinomas follow hyperkeratotic injuries to the skin exposed to the sun.[313]

They occur particularly in blondes; pigmented skins are more resistant to the light. All of the cases studied gave a history of long exposure to the sun and only 3.62 per cent were less than forty years of age. Roffo[314] exposed ten rats to ultraviolet light. Three died within a few days. The remaining rats were exposed to gradually increasing doses for two weeks and then to a continuation of the last dose for seven or eight months. All these animals developed tumors, multiple keratoses, papillomas, carcinomas and sarcomas. The common sites of the tumors were the regions naturally free from hair, such as the ear, the conjunctiva, or regions from which the hair had been removed. In one animal there was a spindle cell sarcoma on one ear and a carcinoma on the other.

On the other hand, Seel and Carls,[315] find ultraviolet irradiation to inhibit the formation of metastases in rabbits injected with the Brown-Pierce sarcoma. It was even able to prolong their lives.

[306] Van Herwerden, M. A., *Protoplasma,* **8,** 413 (1929); *Chem. Abs.,* **25,** 3405 (1931).
[307] Abderhalden, E., and Hartmann, J., *Arch. ges. Physiol. (Pflüger's),* **218,** 261 (1927); *Chem. Abs.,* **22,** 1810 (1928).
[308] Higgins, G. M., and Sheard, C., *J. Exptl. Zoöl.,* **46,** 333 (1926); *Chem. Abs.,* **21,** 3236 (1927).
[309] Enselme, J., and Enselme, J., *Compt. rend.,* **184,** 1353 (1927).
[310] Vles, F., de Coulon, A., and Ugo, A., *Arch. phys. biol.,* **12,** 255 (1935); *Chem. Abs.,* **30,** 1862 (1936).
[311] Roffo, A. H., *Bol. inst. med. exptl. estudio cancer, No. 41,* 4 (1936); *Chem. Abs.,* **31,** 4393 (1937).
[312] Roffo, A. H., and Pilar, F., *J. Physiol. Path. Gen.,* **28,** 854 (1934); *Chem. Abs.,* **25,** 2478 (1931).
[313] Roffo, A. H., *Neoplasmes,* **12,** 257, 521 (1933).
[314] Roffo, A. H., *Ibid.,* **13,** 129 (1934); *Chem. Abs.,* **29,** 507 (1935).
[315] Seel, H., and Carls, H., *Z. Krebsforschung,* **40,** 416 (1934); *Chem. Abs.,* **28,** 3787 (1934).

Miscellaneous Effects on Various Organisms

Henri and Mme. Henri[316] have shown that ultraviolet rays produce involuntary movements in small animals, that a fixed minimum exposure (initial period) is required to produce this effect, and that a definite time (latent period) elapses between the termination of the initial period and the movement. The results show that during the initial period photochemical reactions take place in the peripheral organs and that the products of these reactions are distributed by diffusion and osmosis. The initial and latent periods are not affected by change of temperature. Prolonged exposure to ultraviolet rays renders *Cyclops* immobile, but it responds to ultraviolet rays and the "initial period" is then longer, but gradually returns to its primitive value. This is also the case with an animal in which the nerve terminals have been etherized. The phenomenon of fatigue and the recovery of excitability by ultraviolet radiation, therefore, has its seat in the peripheral organs.

Hinrichs[317] maintains that the amount of irradiation in a given spectral region absorbed by the protoplasm in a given period of time determines whether there is to be an increase or a decrease in the rate of the physiological processes.

The respiration of *Calanus finmarchius* may be increased 100 per cent by light, according to Marshall, Nicholls and Orr.[318]

The photolytic action of light on the luminescent granules of the ctenophore, *Euchoris multicornis,* according to Moore,[319] conforms to the Bunsen-Roscoe law; it proceeds as a first-order reaction and is not accelerated by a rise in temperature.

Recent observations by Kuhn, Moewus and Jerchel[320] indicate that illumination of an aqueous suspension of the gametes of *Chlamydomonas eugamentos* leads to the formation of certain substances which pass into the surrounding solution, and enable it, when added to a dark culture of gametes, to cause them to develop motile flagella and to fuse. These substances may also be destroyed by prolonged exposure of the solutions to light. The motility and development of flagella is produced by red, yellow, green, blue and total visible light, but fusion is produced only by blue and ultraviolet light. These authors have concentrated the motility substance obtained by illumination of gametes with a 500-watt lamp, obtaining it as an orange-yellow dye, which after hydrolysis yielded in chloroform a spectrum similar to that of *trans*-crocetin. The original substance may be a glucoside of crocetin, similar to the crosin of saffron. The fusion substances, different for the male and female gametes, have not yet been concentrated. The precursor is exceedingly sensitive to light. The light-transformed product is an orange-yellow, chloroform-soluble dye with properties similar to those of *trans*-crocetin dimethyl ester. The *cis* form of crocetin dimethyl ester easily rearranges to the *trans* form in blue or violet light.

The absorption spectrum of the porphyrin obtained by extracting the integument of earthworms in darkness is rather rapidly altered by irradiation with light.[321]

Mitogenetic Radiations. In 1923, Gurwitsch[322] claimed that certain biological systems, such as the root tips of onion at certain periods of development, emit radiations in the short ultraviolet which may be detected by their ability to stimulate the growth of other tissues. These rays are called mitogenetic radiations. An extremely large

[316] Henri, V., and Henri, Mme., *Compt. rend.,* **155,** 414 (1912); *J. Chem. Soc.,* **102,** 964 (1912).
[317] Hinrichs, M., *Proc. Soc. Exptl. Med. Biol.,* **26,** 175 (1928).
[318] Marshall, S. M., Nicholls, A. G., and Orr, A. P., *J. Marine Biol. Assoc.,* **20,** 1 (1935); *Chem. Abs.,* **29,** 3045 (1935).
[319] Moore, A. R., *J. Gen. Physiol.,* **8,** 303 (1926).
[320] Kuhn, R., Moewus, F., and Jerchel, D., *Ber.,* **71B,** 1541 (1938).
[321] Kobayashi, S., *Sci., Repts. Tohôku Imp. Univ.,* **5,** 763 (1930); *Chem. Abs.,* **25,** 2489 (1931).
[322] Gurwitsch, L., *Arch. Mikrosk. Anat. u. Entw. Mech.,* **100,** 11 (1923).

number of papers deal with this phenomenon, but as yet its existence can scarcely be said to be established. The radiations are usually stated to lie within the wave-length range of 1900 to 2500A, but to be emitted in such low intensities (about 100 quanta per sq. cm. per second) that only by the use of a Geiger counter could they be physically detected. Some competent observers using this method have failed to detect any evidence of their existence.[323] Most who claim their existence have used biological systems for their detection. In view of the uncertainty which surrounds this field no further discussion will be given here of the more than six hundred recent papers concerning this alleged phenomenon. The reader is referred to the critical reviews of Hollaender and Claus.[324, 325] It is said that the origin is one of several chemiluminescent reactions such as oxidation, glucolysis, hydrolysis, splitting of nucleic acid, etc. It has even been stated that such processes as the setting of plaster of Paris emit ultraviolet rays detectable only by their ability to produce a pigmentation of the skin. Closely related are the necrobiotic rays which Lepeschkin believes to be emitted during the decomposition of constituents of cells which have just died.[326]

[323] Lorenz, E., *U. S. Public Health Repts.*, **48**, 1311 (1933).

[324] Hollaender, A., and Claus, W. D., *J. Opt. Soc. Am.*, **25**, 270 (1935).

[325] Note also the article by Hollaender, A., in Duggar, B. M., "Biological Effects of Radiation," Vol. 2, New York, McGraw-Hill Book Company, Inc., 1936.

[326] Lepeschkin, W. W., *Ber. deut. Bot. Ges.*, **50**, 367 (1932); *Chem. Abs.*, **27**, 316 (1933).

Chapter 37

Therapeutic Applications of Ultraviolet Light Exclusive of Rickets

The health-promoting properties of sunlight have been recognized from the earliest times. The Egyptians treated their sick by exposing them to the sun and the Greeks and Romans had solaria. In the development of medicine, however, actinotherapy received relatively little attention until Finsen in 1893 began a systematic study of the therapeutic uses of light.

Local Therapy. His most notable results were attained in the treatment of lupus (skin tuberculosis) by the rays from a strong carbon arc. Since the source used by Finsen was relatively poor in the effective ultraviolet radiations it was necessary to make prolonged exposures with local pressure for an hour every five days over a period of about six months. The advent of the therapeutic quartz lamp with the improvements described by Kromayer (see Chapter 7) made it possible to shorten the irradiations to but a few minutes. Although Finsen attributed the results to a direct bactericidal action of the rays, it seems, however, that in many cases the bacilli may be lodged too deep for the rays to penetrate to them. Rost, Jessionek and Reyn have suggested that the effect may be indirect since it was found that areas of lupus beyond the immediately irradiated areas also showed improvement.

Dermatologists use this form of treatment for a number of skin diseases other than lupus.[1] The Council of Physical Therapy of the American Medical Association stated that ultraviolet irradiation may produce a favorable effect in the following dermatoses: scrofuloderma, erythema induratum, eczema, psoriasis, parapsoriasis, pustular folliculitis, indolent ulcers, furunculosis, acne vulgaris, angioma serpiginosum, pityriasis rosea. It also is stated that this treatment may induce an attack, cause an exacerbation or produce other injurious effects in the following conditions: eczema, psoriasis, lupus erythematosus, herpes simplex, xeroderma pigmentosum, farmers' skin, and prematurely senile skin. It was held that in some cases the effect of the treatment may be due to a local lethal action upon the superficial diseased cells, which subsequently gradually slough off. In other cases, the effects are due to causes far more complex and as yet but little understood.[2]

Dentists have stated that unfiltered rays from a Kromayer lamp may be employed to advantage in the treatment of sockets after extraction to relieve pain and to promote the formation of new tissue. The usual technique is to precede a one-half to five-minute application of the rays by a thirty-minute application of infrared rays.

Sunlight therapy for local diseased areas was introduced by Bernhard in Switzerland. He states[3] that he first observed the beneficial effects of sunlight

[1] Russell, W. K., *Am. Med.*, **34**, 390 (1928).

[2] American Medical Association, "Handbook of Physical Therapy," 2nd Ed., 1937.

[3] Bernhard, O., cited by Laurens, H., "The Physiological Effects of Radiant Energy," p. 136, New York, The Chemical Catalog Co. (Reinhold Publishing Corp.), 1933.

upon large intractable wounds in 1902. Bernhard attributed the beneficial effects of sunlight to the entire spectrum rather than to just the ultraviolet region. He considered the more penetrating visible and near infrared radiations to stimulate epithelization. The hyperthermia produced by the infrared rays lessens the pain and increases the local circulation. The direct application of the rays of the quartz mercury-arc lamp to wounds not only fails to provide these beneficial radiations but may be deleterious.

Rasero [4] however, claimed that good results followed the irradiation of torpid wounds with the mercury arc, and Coulter and Smith found doses of ultraviolet light which produce a mild erythema on normal skin to aid in the treatment of burns and wounds.[5] They also recommend ultraviolet light in the preparation of infected granulation tissue for skin grafting.

Since the water-cooled Kromayer arc emits a large proportion of its energy as wave-lengths shorter than 3000A, it tends to produce more lethal effects than the air-cooled mercury-arc. The radiations from the water-cooled arc described in Chapter 7 may be applied to areas within the body orifices by means of quartz applicators employing the principle of internal reflections. A wide variety of these, vaginal, prostatic, proctoscopic, nasal, sinus and the like, are available.

General Body Therapy. A more recent development is the general irradiation of large surfaces of the body. Among the most brilliant clinical developments of the past few decades have been those reported by Rollier and others on the use of sunlight in the treatment of tuberculosis of the bones and joints. Since these results were obtained in a clinic opened in 1903 at Leysin in the Alps, at an altitude of 1500 meters, they were attributed to the ultraviolet energy abundant in the solar radiations at those altitudes. As yet, however, there can scarcely be said to be general agreement among those who use the methods of heliotherapy most successfully as to which rays of the sunlight are of the greatest value. The problem is obviously complicated, since factors other than sunlight, such as the effects of altitude, fresh air, rest, adequate diet and other therapeutic measures affect the results attained. Thus it is difficult even to evaluate the part in the cure played by sunlight. There is obviously still a need for much experimental work before it will be known which wave-length regions contribute most to the value of this form of therapy.

That heliotherapy can be successfully employed at sea level has subsequently been demonstrated, notably by Sir Henry Gauvain in England. Gauvain attributed much of the value of heliotherapy at sea level to the frequent variations in intensity which are encountered there. It may be recalled that it had been demonstrated by Laurens and Mayerson that fluctuations in light intensity stimulate various physiological processes. Other successful clinics for heliotherapy at low altitudes have been those of Kisch near Berlin, of Phelps in New Haven at Yale,[6] of LoGrasso at Perrysburg, New York,[7] and one at Chestnut Hills in Pennsylvania, described by Eliason.[8]

At some of these clinics, heliotherapy has been supplemented by the use of artificial light sources, particularly during dark seasons and during the months when the ultraviolet radiations in sunlight are reduced in amount. Reyn supplemented the local treatment of lupus at the Finsen Institute with general body irradiations with

[4] Rasero, R., *Riforma Medica Naples,* **38,** 772 (1922).

[5] Coulter, J. S., and Smith, E. M., Jr., *Radiology,* **16,** 737 (1931).

[6] Phelps, W. M., *J. Bone Joint Surgery,* **12,** 253 (1930).

[7] Mayer, E., "Clinical Application of Sunlight and Artificial Radiation," Baltimore, Williams and Wilkins Company, 1926.

[8] Eliason, R. T., *Annals of Surgery,* **88,** 947 (1928); note also Armand-Delille, P., *J. State Med.,* **43,** 709 (1935).

the carbon arc. Others employ the air-cooled quartz mercury arc for this purpose. Mayer has, for example, stated that peritoneal tuberculosis usually responds to the latter form of treatment. The lethal rays emitted by the mercury arc are reduced considerably in intensity as compared with those of the closely applied water-cooled arc, by the greater distance between the arc and the patient. The present tendency, however, seems toward the use of the carbon arc in solaria for the irradiation of large numbers of patients at one time, since its emission corresponds so much more closely to that of sunlight than does that of the mercury arc. A recent hospital installation is shown in Figure 24 (p. 63).

Because of selective reflection of various spectral regions, consideration must be given to the nature of the reflectors used with either the carbon or the mercury arc. These, if improperly chosen, may alter the quality of the radiant energy emitted by the source. If it is desired to study the relative effectiveness of various spectral regions, provision must be made for the use of suitable filters surrounding the source to isolate various bands of wave lengths.

The intensity on a given skin surface normal to the rays varies approximately as the inverse square of the distance from the arc. This is only a rough statement because the arcs used are not true point-sources of light. The intensity also varies with the cosine of the angle made by the skin surface with the beam of radiant energy. These factors may be considered in calculating the amounts of energy received per square cm. of skin from known values of the energy output of the source under the conditions of operation employed. In practice, however, the energy incident upon the patient may be directly measured by some calibrated apparatus, such as a thermocouple, photoelectric cell, or chemical actinometer.

In determining the dosage in practical therapy, the physician is usually guided, not so much by energy measurements, as by experience with the effects of the source on patients with various types of skin. A test exposure is made to determine the time required to produce a given degree of erythema, and on this is based the dosage to be applied to the body. The erythema test is made on the patient's upper arm, which is covered by a shield cut from a large envelope and containing five small holes. Under this shield is placed a strip of the same material as the shield, which may be withdrawn so as to expose successive areas. A convenient series of exposures permits the irradiation of the areas for times successively doubled from fifteen seconds in the last exposed area to a total of four minutes in the first. These periods are usually suitable for exposures at 36 inches from a bare A-2 National Carbon Co. carbon arc with high-intensity carbons and without a filter glass. In an individual of less than average susceptibility to sunburn, the spot receiving the four-minute exposure shows a visible degree of erythema about forty minutes after the completion of the test and all five spots are clearly visible in less than two hours. Substantial pigmentation results from all exposures but that of fifteen seconds. With the filter glass in place the exposure period required to produce a given degree of erythema is three to four times as long as that required when the same carbons are used without the filter. This method of grading the dosage serves as a safeguard against overexposing areas large enough to cause painful and possibly injurious burns.

The full line curves of Figure 21 (p. 61) show the distance at which the radiation intensity in the wave-length region 2900 to 3100A equals that found in average clinical sunlight for patients at various distances and angles from the filtered carbon arc. The average intensity of that wave-length band in clinical sunlight is taken as 14.5 microwatts per sq. cm. The curves are for high-intensity Sunshine carbons. With high-intensity therapeutic "C" carbons, the intensity will

be over three times the value indicated in the figure. With the filter removed, the intensity of radiations shorter than 3100A will be about 18 times the values shown. The wave-length range specified was chosen for reasons which will become apparent in the discussion of the treatment of rickets in the following chapter.

Several clinicians attempt, in administering general irradiations for systemic effects, to produce a gradual deep tanning of the entire body without causing vesication or undue peeling of the skin. It is scarcely necessary to state that the eyes should be carefully protected during the exposures. Details of the technic should be sought in the detailed reports in the medical literature. It is sound practice to commence by fractional exposures, at each sitting exposing a fresh part and increasing the exposure of previously irradiated regions until the irradiations cover the whole body. This has been the practice of Rollier in heliotherapy, and it finds experimental justification in the work of Levy (1916) and of Gassul (1920), who have shown that general irradiation of the whole body at the first sitting may lead to unfortunate results. Although at one time it was suggested that patients could be sensitized to light to make the treatments more effective by the injection of eosin, such methods are no longer employed.[9]

MacCormac and McCrae[10] have given an account of a serious dermatitis which followed a mercury-arc irradiation of about an hour and ten minutes in the case of a patient who fell asleep during his customary artificial sunbath. After a severe sunburn, there resulted ten days later a severe toxic generalized dermatitis and recovery was delayed for over a month.

There is as yet no general agreement as to the best methods of conducting irradiation therapy. Details of the methods employed and of the results obtained in the treatment of tuberculosis of the bones and joints, peritoneum, intestines, lymph-nodes and genito-urinary system must be sought in the texts of Rollier,[11] of Mayer,[12] and of Russell and Russell,[13] which deal with the experience with this therapy in France, the United States and in England.[14]

There has been one group of workers which holds that pigmentation is necessary to the curative action of ultraviolet rays and that its degree may be regarded as an index of the progress of the cure. A filtering action of the pigment might serve to lessen the lethal action of exposures to intense sunlight at high altitudes where there may be available a very narrow band of radiations of wave-lengths between 2970 and 2910A. However, since most of the pigment is located in the basal cells of the epithelium, and the lethal action occurs in the prickle cells, the pigment could be expected to exert a protective action only upon the deeper tissues which, except in the case of the most intense irradiations, are comparatively slightly affected.

Balderrey and Ewald[15] stated that pigmentation is not merely a protection against the harmful effects of the shortest wave-lengths, but is an important factor

[9] György, P., and Gottlieb, K., *Klin. Wochschr.*, **2**, 1302 (1923); *Chem. Abs.*, **19**, 1600 (1925).

[10] MacCormac, H., and McCrae, H. M., *British Med. J.*, **I**, 693 (1925).

[11] Rollier, A., "Heliotherapy." Translated by de Swietochowski, H. Milford, Oxford University Press, 1927.

[12] Mayer, E., "Clinical Application of Sunlight and Artificial Radiation," Baltimore, Williams and Wilkins Company, 1926.

[13] Russell, E. H., and Russell, W. K., "Ultraviolet Radiation and Actinotherapy," New York, Wm. Wood, 1928.

[14] For more recent reports, see Petter, C. K., *Ann. Internal Med.*, **4**, 1452 (1931); Lehman, A. M., and Bartholomew, D. C., *J. Am. Med. Assoc.*, **98**, 1343 (1932); Willis, H. S., and Cohen, J., *Am. Rev. Tuberculosis*, **23**, 286 (1931); Jessel, G., *Lancet*, **I**, 1182 (1931); Pardee, K., *J. Bone & Joint Surgery*, **12**, 270 (1930); Cox, G. L., *Brit. J. Tuberculosis*, **24**, 1 (1930); *Tubercle*, **12**, 17 (1930); Phelps, W. M., *J. Bone and Joint Surgery*, **12**, 253 (1930); Mayer, E., *Ann. Internal Med.*, **11**, 1856 (1938).

[15] Balderrey, F. C., and Ewald, E., *Am. Rev. Tuberculosis*, **8**, 501 (1924).

in aiding the absorption of visible light, since its presence lessens the reflection from the skin. It also was suggested that the pigmented surface radiates heat at a slightly increased rate and so permits the body to be subjected to longer periods of irradiation without the production of symptoms of insolation.

One school maintains that pigmentation may be produced without visible erythema, provided very carefully graduated doses are employed. Another believes that in the treatment of tuberculosis, doses causing erythema are more productive of beneficial results than are repeated smaller ones. If the views of those who believe the beneficial effects are to be ascribed to the non-specific proteins or protein decomposition products produced by injured cells are held correct, it might be thought necessary to use wave-lengths capable[16] of producing erythema in order to produce the necessary cell injury. If, on the other hand, the beneficial results are due to the formation in the skin of some substance with curative properties, as has from time to time been suggested in analogy with the mechanism of the cure of rickets, then it is conceivable that wave-lengths other than those which cause erythema might suffice. These speculations state problems for the future which will probably best find their solution in well-controlled experiments in large institutions. It would be possible from such experiments to learn definitely which wave-lengths are essential to the curative process and to determine with some degree of accuracy the dosages of energy required at these wave-lengths. Such information would provide a basis for a study of the mechanism by which the therapeutic results are attained—a mechanism regarding which we have at present little more than speculations.

Phelps[17] has asserted that the beneficial results are due to a band of radiant energy lying between 3200 and 3800A. His work could not, however, be corroborated by Luce-Clausen and Bayne-Jones[18] and it has been suggested that his assumption that the sunlight he employed was devoid of rays shorter than 3130A may have been erroneous and that the filters he employed in other experiments may not have completely eliminated the shorter wave-lengths.

Experiments in which guinea pigs were injected intra-abdominally with tubercle bacilli failed in most cases to indicate that irradiated animals were more resistant than the non-irradiated controls.[19] Greenfield[20] found some favorable response in the case of irradiations by direct sunlight in such experiments.

The possibility that the production of vitamin D has a favorable effect on tuberculosis will be considered in the following chapters. As yet opinions are divergent as to the advisability of employing this form of therapy in pulmonary tuberculosis. There is still an opinion held by such workers as Rollier and many others that phototherapy is dangerous in such cases. On the other hand, several recent observers including Potter, Eberson, Cooper and others believe that if caution is used, the treatment may be productive of valuable results.

Jemma[21] states that in twenty children with bone and joint tuberculosis, a lowered alkaline reserve was restored to normal during ultraviolet light therapy. In adult patients, Spence[22] observed a considerable rise in the blood cholesterol after a month of treatment. The greatest rise occurred in those patients who

[16] Peskind, S., *cf.* "Photochemical Immunization: Autogenous Vaccination Through Irradiation," S. P. Mount & Co., Cleveland, 1934.

[17] Phelps, W. M., *J. Bone and Joint Surgery*, **12**, 253 (1930).

[18] Luce-Clausen, E. M., and Bayne-Jones, S., *Am. Review Tuberculosis*, **24**, 686 (1931).

[19] Steinbach, M. M., Hess, A. F., and Weinstock, M., *Am. Rev. Tuberculosis*, **22**, 35 (1931).

[20] Greenfield, M., *Am. Rev. Tuberculosis*, **24**, 695 (1931).

[21] Jemma, G., *Pediatria Revista*, **36**, 878 (1928); *Chem. Abs.*, **22**, 4620 (1928).

[22] Spence, C., *Brit. J. Actinotherapy*, **3**, 148 (1928); *Chem. Abs.*, **23**, 858 (1929).

showed clinically the greatest improvement. No significant changes in the calcium and phosphorus levels were observed.

With the demonstration of the value of ultraviolet therapy in the treatment of tuberculosis and of rickets (see Chapter 38), irradiation came to be used with varying results in a wide variety of diseases. The literature is replete with claims for its efficacy in conditions ranging from mental diseases through whooping cough to bronchial asthma. Unfortunately, the results obtained have not been such as to sustain the enthusiasm with which the method was lauded. Illogical attempts to utilize ultraviolet light for conditions for which there is little theoretical or experimental foundation met with failure and caused many physicians to discard expensive equipment.

The physiological studies reviewed in the preceding chapter reveal few responses to ultraviolet light which may serve as a basis upon which to build a rational therapy. Studies of the irradiation of abnormal or diseased subjects have given, at least in the case of rickets, more promising results. It might be thought that the reduction in blood pressure to which reference has been made in the preceding chapter might serve as a basis for expecting irradiation to give results in the treatment of hypertension. Indeed, some favorable responses to this treatment were recorded by Laurens in a study of a series of cases of essential hypertension. Others, however, proved entirely refractory. Marx [23] reported rather favorable results in a series of 21 ambulant, hypertension patients, using carbon filament lamps. With the carbon arc, Bach [24] found that in 105 observations on 19 men and 10 women, the blood pressure fell during irradiation in 101, showed no change in 2 and increased slightly in 2 observations. The decreases averaged 7.2 mm; the largest was 17 mm. With the quartz mercury arc, Koenigsfeld [25] observed decreases of from two to eight mm. immediately after irradiation. In eclampsia, Hochenbichler [26] obtained marked decreases in blood pressure, but frequently it rose again shortly after the treatment. The probability is that dilatation of the skin vessels produces a transient lowering of the blood pressure and causes some decongestion of blood from the internal organs.

The results in anemias have not in general been encouraging, although some favorable results in pernicious anemia were reported from the Taft Heliotherapy Ward at the Cincinnati General Hospital.[27]

There is a widespread impression that the employment of ultraviolet light in treating patients with diabetes is dangerous. This is in part based upon observation by Sampson [28] and by McCaskey.[29] From the fact, however, that the blood sugar is commonly reduced somewhat during irradiation, it seems that there is little if any foundation for this contention. Indeed, some workers, such as Faber and Bloch,[30] have obtained encouraging results in its use in the treatment of diabetic children. Grayzel, Collens and McKenzie [31] found it to have no effect on the sugar balance of such patients.

That ultraviolet irradiation should increase the resistance of the skin to infection was a natural suggestion from the results of local therapy. Rollier noted that

[23] Marx, H., *Klin. Wochschr.*, **7**, 795 (1928).
[24] Bach, H., *Deut. Med. Wochschr.*, **37**, 401 (1911).
[25] Koenigsfeld, H., *Z. Klin. Med.*, **91**, 159 (1921).
[26] Hochenbichler, A., *Centralbl. Gynäkol.*, **51**, 1649 (1927).
[27] Friedlander, A., and Wiedemer, C., *Arch. Internal Med.*, **44**, 209 (1929).
[28] Sampson, C. M., "Physiotherapy Technique," C. V. Mosby, St. Louis, 1923.
[29] McCaskey, D., *New York Med. J.*, **109**, 504 (1919).
[30] Faber, F., and Bloch, C. E., *Am. J. Diseases of Children*, **30**, 504 (1925).
[31] Grayzel, H. G., Collens, W. S., and McKenzie, M. R., *Am. J. Diseases of Children*, **38**, 513 (1929).

the eruptions of chicken pox are slighter than usual in patients with pigmented skin. Hyde and LoGrasso found that skin infections occurred but rarely in pigmented patients, and Carnot, Camus and Benard found that in rabbits irradiated before inoculation with vaccine virus, the development of an eruption was prevented.[32]

That the blood should also become increasingly bactericidal as a result of the generalized irradiation of a patient has been occasionally suggested. Colebrook, Eidinow and Hill [33] have given some evidence for a temporary increase in the bactericidal power of the blood following a single exposure to the mercury arc. Robertson [34] believed that solar or mercury-arc irradiation of rats raised their resistance to infection with *B. coli communis*. Blasi [35] found that the opsonic index of the blood serum of children with a positive von Pirquet test toward the tubercle bacillus was increased after ten irradiations with the mercury arc. Hansen found that carbon arc baths applied to 230 patients who had received single injections of dead typhoid bacilli increased the formation of agglutinins in their blood. He believed the effect due to the heat of the deeply penetrating infrared rays. In general, however, immunological experiments (described in the preceding chapter) have given little foundation for a belief that irradiation increases resistance.

Many have suggested that generalized irradiations might protect people from the common cold. Maughan and Smiley at Cornell [36] conducted a series of experiments on students, in which 23 received full mercury-arc treatments at 30 inches, the arc being operated at 4 amperes and 130 volts. The entire posterior and anterior surfaces of the body received the rays for five minutes, the treatments being given weekly for about nine weeks. 58 controls were used. During this period the number of colds per individual treated was 1.48 and per individual untreated 2.48. These workers ascribed the failure of others to reduce the incidence of colds by this method to overdoses. In a second series, in one twelve-week period the results were 1.56 and 2.80 colds in the treated and untreated subjects. A second period of nine weeks showed 1.24 and 2.79, respectively. The subjects used were selected as being especially prone to suffer colds.

These results were, however, contradicted by the work of Doull, Hardy, Clark and Herman [37] who also used mercury arcs and gave light or moderate doses which produced only a minimal erythema. The total incidence was found to be slightly higher in the irradiated patients receiving more than ten treatments than in the controls. The cases occurring in the irradiated group also appeared to be somewhat more severe than those in the non-irradiated subjects.

Barenberg, Friedman and Green,[38] found that irradiation did not protect infants from whooping cough, chicken pox or respiratory infections. Both the carbon arc and the mercury arc were used. In children the evidence from blood counts showed, according to Gonce and Kassowitz [39] no enhanced bactericidal property in the blood after ultraviolet irradiation. They concluded that in the majority of their patients, particularly if they were the hosts of an infection, daily quartz lamp

[32] See also Rivers, T. M., Stephens, H., and Gates, F. L., *J. Exptl. Med.*, **47**, 37, 45 (1928).
[33] Colebrook, L., Eidinow, A., and Hill, L., *Brit. J. Exptl. Path.*, **5**, 54 (1924); Eidinow, A., *Lancet*, **II**, 963 (1927); *Med. J. and Record*, **130**, 695 (1929).
[34] Robertson, E. C., *Can. Med. Assoc. J.*, **19**, 154 (1928); Robertson, E. C., and Ross, J. R., *Proc. Soc. Exptl. Biol. Med.*, **27**, 999 (1930).
[35] Blasi, D., *Clinica Pediatrica*, **11**, 832 (1929).
[36] Maughan, G. H., and Smiley, D. E., *J. Preventive Med.*, **2**, 69 (1928); *Am. J. Hygiene*, **9**, 466 (1929).
[37] Doull, J. A., Hardy, M., Clark, J. H., and Herman, N. B., *Am. J. Hygiene*, **13**, 460 (1931).
[38] Barenberg, L. H., Friedman, I., and Green, D., *J. Am. Med. Assoc.*, **87**, 1114 (1926); Barenberg, L. H., and Lewis, J. M., *Ibid.*, **90**, 504 (1928).
[39] Gonce, J. F., and Kassowitz, K., *J. Am. Med. Assoc.*, **90**, 280 (1928).

irradiation led to a lowered bactericidal power of the blood. The opposite effect was obtained in a few cases. Similar observations are due to Colebrook.[40] Hardy and Chapman, who studied the effect of irradiation on the ability of rabbits to resist *Bacillus leptisepticum,* found light doses to have little effect and heavy doses to be harmful. According to Petrie,[41] the susceptibility of guinea pigs to spontaneous pneumococcus infection was not affected by irradiation. Negative results were also reported by Hill, Greenwood and Topley[42] in an extensive experiment on the effects of exposure under normal conditions on the resistance of over a thousand mice to *Pasteurella* infection.

In the annual report of the Medical Research Council of London for 1927-8, it is stated that heavy expenditures for Vita-glass or other ultraviolet-transmitting glasses for school rooms or for expensive irradiation equipment for schools has not been justified. Under the auspices of the Council, Dr. Dora Colebrook arranged an elaborate test of the value of lamp therapy, the results of which were entirely negative. Her experiment, however, has been criticized, notably by Hill and Laurie,[43] who felt that the control children had been unwisely selected in that they lived in a district where the hygienic conditions and the available sunlight had been adequate. Their own observations indicated that irradiation improved the appetite and sleep of a group of children. The Council on Physical Therapy of the American Medical Association has stated that as far as normal persons are concerned the claim that exposure to ultraviolet rays increases or improves the tone of the tissues or of the body as a whole, stimulates metabolism or tends to prevent colds has not been conclusively substantiated.

Thus it would seem that opinions are still divergent in regard to the value of generalized irradiations on the general health and resistance to disease. This is a particularly difficult subject to investigate objectively. General reports of feelings of exhilaration or invigoration cannot be appraised scientifically. In contrast to this, the value of irradiation on the prevention of rickets is definitely confirmed and well understood.

There is some evidence that irradiation has a beneficial effect in bronchial asthma, at least in children.[44] In hay fever, hyperesthetic rhinitis and the asthmas, investigations by Novak and Hollaender[45] indicated favorable results attributed to an influence exerted upon the blood calcium which tended to be low in these conditions. Favorable effects of ultraviolet therapy given in conjunction with calcium salts in epilepsy have been reported by Borrows.[46]

Roskin and Romanova[47] find that non-therapeutic doses of novarsolan given with ultraviolet irradiations have no effect on malaria in canaries although they are effective in mice. The serum of irradiated mice has the property of increasing the therapeutic action of novarsolan, neoarsphenamine and novarsenol in the malaria of canaries, presumably because of the passive transfer of some necessary factor. Although Roskin and others claimed[48] that irradiation synergizes the trypanocidal action of neoarsphenamine, Giemsma and Ellenbogen[49] could not confirm such an action. Negative results have

[40] Colebrook, L., *Brit. Med. J.*, **2,** 11 (1924).

[41] Petrie, G. F., *J. Hygiene,* **30,** 154 (1930-31).

[42] Hill, L., Greenwood, M., and Topley, W., *Brit. J. Exptl. Path.*, **11,** 182 (1930).

[43] Hill, L., and Laurie, A. R., *Lancet,* **I,** 182 (1931).

[44] Saidman, J., *Arch. Med.-Chir. l'App. Respiratoire,* **3,** 480 (1929).

[45] Novak, F. J., and Hollaender, A. R., *J. Am. Med. Assoc.,* **81,** 2003 (1923); *Chem. Abs.,* **18,** 1153 (1924).

[46] Borrows, P. J., *U. S. Veterans Bureau Med. Bull.,* **7,** 661 (1931); *Chem. Abs.,* **26,** 2245 (1932).

[47] Roskin, G., and Romanova, K., *Z. Immunitäts.,* **82,** 461 (1934); *Chem. Abs.,* **28,** 7361 (1934); *Z. Immunitäts.,* **62,** 147, 158 (1929); **72,** 445 (1931); **67,** 94 (1930); *Chem. Abs.,* **25,** 3080 (1931).

[48] Roskin, G., Bichowskaja, A., and Schischliaiewa, S., *Z. Immunitäts.,* **67,** 91 (1930); Roskin, G., *Ibid.* **69,** 240, 473 (1930); **63,** 452 (1929); *Chem. Abs.,* **25,** 3080 (1931).

[49] Giemsma, G., and Ellenbogen, V., *Z. Immunitäts.,* **67,** 78 (1930); *Chem. Abs.,* **25,** 3080 (1931); positive results have been reported by Marzinovskii, E. J., *Z. Immunitäts.,* **74,** 379 (1932) and by Orlov, S., and Levinson, L., *Ibid.,* **78,** 264 (1933); *Chem. Abs.,* **27,** 5422 (1933).

also been reported for the effects of ultraviolet irradiation on the splenic anemia of kala-azar by Morabito,[50] although in the anemias of luetic or tuberculous origin the results were more favorable.

Attempts have been made to treat mastitis in cows by ultraviolet irradiations, but Gildow, Hansen and Cherrington[51] found no consistent reduction in the number of bacteria or of the leucocytes in the middle milk of cows with subacute or chronic mastitis after such treatment. Ultraviolet treatment has also been proposed for distemper in dogs.[52]

Von Fellenberg[53] was unable to obtain evidence that ultraviolet irradiation had any effect upon endemic goiter. The weight and the iodine content of the thyroid are the same in rats reared in direct sunlight and in those reared in darkness.[54] Smith,[55] however, believes that a lack of sunlight may result in a deficiency of iodine in the thyroid gland and notes a relationship between a lack of irradiation and endemic goiter in the United States, India and New Zealand. In the last-named region the iodine content of the soil seems to be proportional to the solar radiations and similar observations have been made in regard to variations in the iodine content of potatoes grown in South Carolina.

[50] Morabito, F., *Pediatria Revista,* **35,** 1112 (1927); *Chem. Abs.,* **22,** 1801 (1928).

[51] Gildow, E. M., Hansen, H. C., and Cherrington, V. A., *J. Am. Vet. Med. Assoc.,* **35,** 55 (1933); *Chem. Abs.,* **27,** 1399 (1933).

[52] For other applications in veterinary medicine, see Patton, J. W., *J. Am. Veterinary Med.,* **69,** 734 (1926).

[53] Von Fellenberg, T., *Biochem. Z.,* **235,** 205 (1935).

[54] But see Bergfeld, W., *Endokrinologie,* **6,** 269 (1930); *Chem. Abs.,* **24,** 3552 (1930).

[55] Smith, J. H., *Arch. Internal Med.,* **50,** 76 (1932).

Chapter 38

Rickets and Irradiation

Rickets is a common disease of infants and young children. It consists chiefly in a faulty deposition of calcium in the extremities of the long bones. The clinical picture is thoroughly discussed in a book by Hess [1] which also includes a critical discussion of the flood of papers which appeared subsequent to 1919 regarding the importance of vitamin D in this condition and the relation of sunlight to the production of this vitamin in the skin. The disease is accompanied by disturbances in calcium or phosphorous metabolism. It is usually characterized by low values of either or both calcium and phosphorus in the blood serum.

In 1909, the pathological studies of Schmorl [2] brought to light an interesting seasonal variation in the incidence of the disease. There is a high incidence of rickets in winter and the healing of the disease, slight in winter, reaches its maximum in summer. Not for some time, however, were attempts made to correlate these data with the seasonal variations of the intensity of sunlight, although it is true that an Englishman, Palm, had suggested as early as 1890 [3] that the chemical activity of the sun's rays may play an important part in the therapy of this disease. An experiment by Raczynski [4] attracted little attention. He kept one puppy in sunlight and another of the same litter in darkness for six weeks. At the end of this period, the body of the first was found to contain much more calcium and phosphorus than did that of the second. Bernhard in 1917 also drew some conclusions as to the influence of sunlight on the incidence of rickets in the children of certain Alpine villages.

Apparently the first definite statement that the irradiation of a rachitic child with ultraviolet rays would bring about a cure was published by Huldschinsky in 1919.[5] His paper contained a number of Röntgenograms which indicated beyond any doubt that the epiphyses of the long bones of rachitic infants undergo rapid calcification following the exposure of their bodies to a mercury-vapor lamp.

Clinical observations by Hess and Unger a year previously had indicated that such irradiations might have a slight effect in decreasing the size of the enlarged costo-chondral junctions, the so-called rachitic rosary, a diagnostic sign of rickets. They attached little significance to this, however, for in 1920 they stated that children in glass cubicles receiving a liberal supply of light nevertheless became rachitic and were not benefited by ultraviolet light treatments.[6] A year later, however, they published a preliminary note on the cure of rickets by sunlight [7] in which they employed the expression "encouraged by our results in curing rickets by means of the ultraviolet ray." At this time they also attributed the seasonal

[1] Hess, A. F., "Rickets, Osteomalacia and Tetany," Philadelphia, Lea and Febinger, 1929.

[2] Schmorl, G., *Ergeb. der Inn. Med. u. Kinderheilk,* **4,** 403 (1909); cited in Hess, A. F., "Rickets, Osteomalacia and Tetany," Philadelphia, Lea and Febinger, 1929.

[3] Palm, T. A., *Practitioner,* **45,** 270, 321 (1890).

[4] Raczynski, J., *Compt. rend. assoc. intern. pediat.,* 308 (1912); cited in Hess, A. F., "Rickets, Osteomalacia and Tetany," Philadelphia, Lea and Febinger, 1929.

[5] Huldschinsky, K., *Deut. Med. Wochschr.,* **45,** 712 (1919).

[6] Hess, A. F., and Unger, L. J., *J. Am. Med. Assoc.,* **74,** 217 (1920).

[7] Hess, A. F., and Unger, L. J., *J. Am. Med. Assoc.,* **77,** 39 (1921)

variations in the incidence of the disease to the seasonal variations in the intensity of sunlight.[8]

The further study of this disease was promoted by the discovery that it could be produced in experimental animals by the use of deficient diets, particularly those low in phosphorus.[9] It was soon shown that animals receiving a diet either low in phosphorus and high in calcium or one low in calcium and high in phosphorus developed symptoms of rickets. They could be protected from the effects of the diet by daily exposures to sunshine of only fifteen minutes, except in winter when longer exposures were required. The demonstration that light filtered through a window of ordinary glass was ineffective showed that only the ultraviolet portion of the solar spectrum was important. Only short periods of exposure to ultraviolet sources were required for protection against the defective diets. With the quartz mercury lamp a daily irradiation of three minutes at a distance of three feet was adequate. These effects on the growth and skeletal calcification of the rats were similar to, if not identical with, those brought about by sunshine or by the addition of cod-liver oil to the diet. Cod-liver oil was the remedy in most frequent use in the treatment of rickets.[10]

These results were quickly confirmed on many sides [11] and the curative results of carbon-arc treatments also were observed.[12] During the treatment the inorganic phosphates of the blood increased, and the signs of the disease subsided. Preadministration of phosphates hastened the cure, although addition of dipotassium hydrogen phosphate in the absence of irradiation was unsuccessful in clinical cases.

The next important advance was the demonstration that the light acts by a chemical mechanism. Hess and Weinstock [13] showed that a section of excised human skin after irradiation by a mercury arc when fed to rats, protected them from a deficient diet, although similar amounts of nonirradiated skin were ineffective. It was thus obvious that an antirachitic substance had been formed photochemically in the irradiated skin. This was later confirmed by Falkenheim,[14] who also showed that the irradiation of but one portion of the skin of a rat produces antirachitic properties in other portions of the skin, although to a less extent than in the directly irradiated area. This observation implied that some of the active agent produced in the skin may be absorbed by the blood and distributed to other portions of the skin. As late as 1926, however, Bloch and Faber [15] denied the existence of the hypothetical antirachitic material, although they admitted that ultraviolet light had a curative action on the disease. Hume, Lucas and Smith [16] showed that normal calcification could be produced in rachitic rabbits by irradiating an area of skin as small as 2.5 by 3.5 cm. for only ten minutes three times a week, a proof of the extraordinary effectiveness of the unknown material formed in the skin.

It has been stated that cod-liver oil had been known for some time to contain a substance exerting a similar curative effect upon rickets and the question natu-

[8] Hess, A. F., and Unger, L. J., *Am. J. Diseases of Children,* **22,** 186 (1921).

[9] Hess, A. F., Unger, L. J., and Pappenheimer, A. M., *J. Biol. Chem.,* **50,** 77 (1922); *J. Exptl. Med.,* **36,** 437 (1922); Hess, A. F., and Gutman, M. B., *J. Am. Med. Assoc.,* **78,** 29 (1922).

[10] Powers, G. F., Park, E. A., Shipley, P. G., McCollum, E. V., and Simmonds, N., *Proc. Soc. Exptl. Biol. Med.,* **19,** 120 (1921).

[11] Schultzer, P., and Sonne, C., *Acta Med. Skand., Suppl.,* **VII,** 97 (1924); Eckstein, A., *Arch. Kinderheilk.,* **74,** 1 (1924); *Chem. Abs.,* **18,** 3207 (1924).

[12] Hess, A. F., and Unger, L. J., *J. Am. Med. Assoc.,* **78,** 1596 (1922).

[13] Hess, A. F., and Weinstock, M., *J. Am. Med. Assoc.,* **80,** 687 (1922).

[14] Falkenheim, C., *Klin. Wochschr.,* **5,** 2071 (1926).

[15] Bloch, C. E., and Faber, F., *Am. J. Diseases Children,* **30,** 504 (1926).

[16] Hume, E. M., Lucas, N. S., and Smith, H. H., *Biochem. J.,* **21,** 362 (1927).

rally arose as to whether this might be identical with the material formed during the irradiation of skin. For several years it had been recognized, in large part because of the work of Mellanby, that cod-liver oil contains fat-soluble vitamins essential to the normal development of animals. But for a time it was not recognized that there are at least two fat-soluble vitamins in cod-liver oil. The investigations by which it was established that one of these, vitamin A, is concerned primarily with growth and the prevention of xerophthalmia, and that another, vitamin D, is concerned with the prevention of rickets, lie for the most part beyond the scope of our subject matter.

As early as 1922, Hume[17] showed that rats on a vitamin A-deficient diet could not be protected from the effects of the lack of this vitamin by irradiation if the experiment was continued for a sufficient period. It followed that this vitamin is not produced in the animal as a result of photochemical processes. This was also the conclusion of Goldblatt and Soames[18] from independent experiments. Sheets and Funk[19] similarly found that on a diet deficient in fat-soluble vitamins (then called incorrectly vitamin A) a three- to five-minute daily irradiation by ultraviolet light prevented the appearance of rickets and, although the rate of growth of the animals was normal, xerophthalmia developed. Powers, Park and Simmonds[20] clearly recognized the existence of two separate factors or vitamins in cod-liver oil, the antixerophthalmic A and the antirachitic D.

It was next shown by Goldblatt and Soames[21] that so long as the necessary vitamins are supplied in the diet light is not essential. Other experiments prior to the recognition of vitamins A and D as separate entities were by Eckstein.[22]

Steenbock and Nelson[23] found that such antirachitic agents as ultraviolet rays or cod-liver oil would restore the growth of rats maintained on a diet deficient in the fat-soluble vitamins but would not postpone the onset of xerophthalmia. They viewed these results as supporting the view that cod-liver oil contains two vitamins. It was also shown that non-irradiated rats receiving a diet deficient in the antirachitic factor showed normal growth when placed in the same cage with irradiated rats on the same diet. The same effect was obtained when the rats were placed in a jar on a galvanized iron wire screen contaminated slightly by other rats having been kept on them and then irradiated. It was necessary that the rats have access to the irradiated screen in order that they might ingest traces of excreta or skin secretions which had been irradiated. Irradiated air had no beneficial effects.[24]

Effective Wave-Length Regions

Once the effects of ultraviolet light in preventing the development of rickets had been established, the physical aspects of the process were studied to learn more precisely which wave-lengths are effective. Pappenheimer and Weinstock,[25] by interposing standard glass filters, found that wave-lengths as long as 3340A had no protective action, the effective rays being in the neighborhood of 3130A. Hess and Weinstock[26] thought the wave-length must not be longer than 3130A and found the effectiveness of the 3020A line very great. Mouriquand, Bernheim and

[17] Hume, E. M., *Lancet*, **II**, 1318 (1922).
[18] Goldblatt, H., and Soames, K. M., *Lancet*, **II**, 1321 (1922).
[19] Sheets, O., and Funk, C., *Proc. Soc. Exptl. Biol. Med.*, **20**, 80 (1922); *Chem. Abs.*, **17**, 3528 (1923).
[20] Powers, G. F., Park, E. A., and Simmonds, N., *Proc. Soc. Exptl. Biol. Med.*, **20**, 81 (1922).
[21] Goldblatt, H., and Soames, K. M., *Biochem. J.*, **17**, 294, 622 (1923).
[22] Eckstein, A., *Arch. Kinderheilk.*, **73**, 1 (1923); Allenbach and Simon, R., *Rev. Hyg. Soc. Strasburg*, **81**, 670 (1923); *Bull. Soc. Hyg. Aliment.*, **11**, 124 (1923); *Chem. Abs.*, **17**, 2306 (1923).
[23] Steenbock, H., and Nelson, M. T., *J. Biol. Chem.*, **56**, 355 (1923); see also *Ibid.*, **62**, 575 (1925) and Steenbock, H., Nelson, M. T., and Black, A., *Ibid.*, **62**, 275 (1924).
[24] For further discussion of the separate assay of vitamins A and D on rats see Dutcher, R. A., and Kruger, J. H., *J. Biol. Chem.*, **69**, 277 (1926) and Sherman, H. C., and Hessler, M. C., *J. Biol. Chem.*, **73**, 113 (1927).

Theobalt[27] observed that rats irradiated five minutes daily by a mercury arc with an interposed Wood's glass filter developed rickets, but that those receiving 90 minutes of irradiation under these conditions did not. Luce[28] found that a filter transmitting 5 per cent of the incident light at 3050A and cutting off completely at 2960A destroyed the effectiveness of irradiation, but that a screen transmitting 80 per cent at 3000A and letting through some rays to 2400A, and one transmitting 77 per cent at 3000A and cutting off between 2650 and 2450A, each transmitted the effective rays. Hess and Weinstock[29] believed that wave-lengths shorter than those available in sunlight had even greater potency. They noted during the winter months when the shorter wave-lengths do not reach the earth, and even the longer ones reach it with lowered intensity, that the effective wave-lengths available are reduced to a band only about 50A wide, between 3130 and 3080A. Maughan[30] found the wave-length 2968A four times as effective as 3020A.

Huldschinsky[31] once proposed to term rays of wave-length longer than 3200A, ultraviolet A, those between 3200 and 2890A ultraviolet B (standing for biologically active), and those shorter than 2890A, ultraviolet C. This suggestion failed to find general favor.

Bunker and Harris[32] advocated an attitude of caution in regard to the acceptance of the view that only a narrow band near 3000A is of importance.

Amounts of Energy Required

Recent studies indicate that the most effective wave-length for curing rickets in rats is 2804A.[33] To produce healing equivalent to that due to one international unit of vitamin D, the following energies (in thousands of ergs) were required at various wave-lengths: 2653A, 287; 2804A, 226; 2894A, 395; 2967A, 280; 3024A, 553; 3128A, 27,545. Prolonged irradiation, particularly by the shorter wave-lengths 2653, 2804 and 2894A has a destructive action. Stein and Lewis[34] found that at Denver, direct sunlight in June and July was effective for rats in exposures as short as 3.75 minutes daily. Curative effects are produced in either chickens or human infants by irradiation by even, in some cases, tungsten filament lamps in thin Corex D glass bulbs, according to Maughan and Dye,[35] and Gerstenberger and Horesh.[36] In the case of the children, continuous exposures were given for twelve hours to two lamps six feet apart housed in oxidized aluminum reflectors five and a half feet above the bed level. Hauch and Hanke[37] found that February sunlight at the street level in Chicago failed to protect rats on a rachitic diet and exposed behind commercial ultraviolet glasses. Under the same conditions, however, they were protected fully by March to April sunlight. Control rats behind ordinary glass were not protected.

[25] Pappenheimer, A. M., and Weinstock, M., *Proc. Exptl. Biol. Med.*, **20**, 14 (1922).
[26] Hess, A. F., and Weinstock, M., *J. Am. Med. Assoc.*, **80**, 687 (1922).
[27] Mouriquand, G., Bernheim, M., and Theobalt, Mlle., *Compt. rend.*, **182**, 1490 (1926).
[28] Luce, E. M., *J. Biol. Chem.*, **71**, 187 (1926).
[29] Hess, A. F., and Weinstock, M., *J. Am. Med. Assoc.*, **89**, 1222 (1927).
[30] Maughan, G. H., *Am. J. Physiol.*, **87**, 381 (1928).
[31] Huldschinsky, K., *Klin. Wochschr.*, **5**, 1972 (1926).
[32] Bunker, J., and Harris, R., *Am. J. Public Health*, **20**, 1278 (1930).
[33] Knudson, A., and Benford, F., *J. Biol. Chem.*, **124**, 287 (1938).
[34] Stein, H. B., and Lewis, R. C., *Am. J. Diseases of Children*, **41**, 62 (1931).
[35] Maughan, G. H., and Dye, J. A., *J. Opt. Soc. Am.*, **20**, 279 (1930); *Proc. Soc. Exptl. Biol. Med.*, **28**, 106 (1930).
[36] Gerstenberger, H. J., and Horesh, A. J., *J. Am. Med. Assoc.*, **96**, 766 (1931).
[37] Hauch, J. T., and Hanke, M. E., *Ind. Eng. Chem.*, **23**, 1398 (1931).

In New Orleans, Mayerson and Laurens[38] found the following to be the minimal daily times of irradiation necessary: February and March, 3 to 5 minutes for chicks and 5 to 6 minutes for rats. For either, the times were from April through October, 3 to 5 minutes, and from November through January, 5 to 6 minutes. The average daily amount of direct solar radiation of wave-length shorter than 3130A that will prevent rickets in rats is less than 0.001 calorie per sq. cm. from April to October, and between 0.001 and 0.002 calorie during the rest of the year. Of course, it is necessary to consider the number of sq. cm. exposed at such intensities since there is a minimal dose of vitamin D which must be produced in the total irradiated area for the protective action to become effective. For the prevention of leg weakness in chicks the amount of energy required was found to be about 0.00069 calorie per sq. cm. daily.

Children need have only a small portion of their bodies irradiated for successful results. Thus Catel[39] found it necessary to irradiate only the face or any area of 90 sq. cm.

There have been several other studies of the effectiveness of winter sunshine at various geographical locations. Tisdall and Brown,[40] working at Toronto, found that a marked increase in the antirachitic effect of sunshine occurs whenever the sun reaches an altitude of 35° or more. Geographically, rickets is uncommon or exists in but a mild form in those places where the minimal seasonal altitude of the sun is not below this angle, and severe rickets is chiefly encountered in those cities where the altitude is below that value for some months of the year. At Toronto, the antirachitic effect of the skyshine was about one-half to two-thirds as great as that of sunshine, by which is meant both the direct rays from the sun and the rays reflected from the sky and clouds. Even December skylight had a definite antirachritic effect. Fleming[41] found that at Washington, D. C., the winter sunlight is antirachitic for rats after passing through Vitaglass. Under the same conditions, north skylight was also protective during the months of April, May, June and July. At Boston, Wyman[42] found it possible to cure rickets in the winter months by exposures to sunlight through quartz windows or Corning glass windows, although the results were less favorable with Vitaglass. (See Chapter 10.) Favorable results were obtained also by means of Cel-O-Glass windows.[43] Jendrassik and Papp[44] found that at Budapest the sunlight was ineffective during December and January. Its activity then rose to a sharp and high peak at mid-June and declined again practically at the same rate.

A painstaking investigation of the energy required is that of Sonne and Rekling,[45] who employed a monochromator and determined by means of a thermopile the energy in gm. calories per sq. cm. incident at each of several wave-lengths on an area of the experimental animals of 8.1 sq. cms. In this way it was possible to eliminate the relative intensities of the various lines emitted by the source. The effect of the 3130A line was doubtful, although the incident energy amounted to $4.3\times0.708\times10^{-4}$ gm. cal. per sq. cm. per minute. At 3020 to 2970A with a somewhat lower intensity ($3\times0.708\times10^{-4}$ gm. cal. per sq. cm. per minute) there was a strong antirachitic action. This was also the case at 2650A, although the intensity was lower, $1.5\times0.708\times10^{-4}$ gm. cal. It was also

[38] Mayerson, H. S., and Laurens, H., *Am. J. Physiol.*, **102**, 422 (1932).

[39] Catel, W., *Monatschr. Kinderheilk.*, **54**, 426 (1932); *Chem. Abs.*, **27**, 2184 (1933).

[40] Tisdall, F. F., and Brown, A., *Can. Med. Assoc. J.*, **20**, 253 (1929); *Chem. Abs.*, **23**, 3007 (1929); *Am. J. Diseases of Children*, **34**, 721, 737, 742 (1927); **36**, 734 (1928); *J. Am. Med. Assoc.*, **92**, 860 (1929); **94**, 854 (1930).

[41] Fleming, W. D., *Military Surgeon*, **62**, 592 (1928); **63**, 658 (1928).

[42] Wyman, E. T., *Boston Med. & Surg. J.*, **197**, 376 (1927).

[43] Wyman, E. T., Drinker, P., and Mackenzie, K. H., *Am. J. Diseases of Children*, **39**, 969 (1930).

[44] Jendrassik, A., and Papp, S., *Biochem. Z.*, **268**, 364 (1934). In these experiments ergosterol rather than patients or experimental animals was irradiated.

[45] Sonne, C., and Rekling, E., *Strahlentherapie*, **25**, 552 (1927); cited by Laurens, H., "The Physiological Effects of Radiant Energy," New York, The Chemical Catalog Co., Inc. (Reinhold Publishing Corp.), 1933.

strong at 2530A where the intensity was slightly greater, $1.6\times0.708\times10^{-4}$ gm. cal. On the other hand, at 2480 and at 2390A where the energies were respectively 0.7 and $0.55\times0.708\times10^{-4}$ gm. cal. per sq. cm. per minute, there was but slight action. No protection was afforded by the wave-lengths 2270 to 2200A, with $0.4\times0.708\times10^{-4}$ gm. cal. per sq. cm. per minute.

The opinions of workers who have studied the influence of the pigment of the skin on the curative effects of sunlight differ somewhat. Schultzer and Sonne and Hess, and Unger and Pappenheimer believe that pigmentation in rats somewhat lessens the effects of irradiation. In children, however, Kramer, Casparis and Howland, as well as Levinsohn,[46] conclude that the skin pigment of the Negro child does not interfere with the action of ultraviolet rays.

Gerstenberger and Hartman[47] found that quartz lamp exposures weekly with doses of one erythema unit for negro infants, and less for white infants, applied to both front and back, caused healing in practically the same time as did heavier doses. Gerstenberger and Russell[48] obtained similar results with the General Electric Sunlamp S-1. Using a quartz lamp at 80 cm., Vollmer found a weekly dose of from four to five minutes each to the chest and back to be the minimal effective dose. Cures were effected after the application of about 100 minutes of treatment.

Effects on Mineral Metabolism.

Ultraviolet irradiation cannot overcome mineral deficiencies of the diet. Its function is to supply the vitamin D necessary to control the proper utilization of the calcium and phosphorus in the diet. Theiler[49] emphasized the fact that when the phosphorus of the diet of cattle is deficient rickets will develop in the presence of abundant solar radiations. Many papers have been devoted to the effects of irradiation upon the blood phosphorus and calcium levels during the cure of rickets. In contrast to the negative results discussed in the preceding chapter in regard to the influence of irradiation upon these values in the normal individual, there is general agreement that if the mineral contents of the diet are suitable, the low values which characterize rickets are readily restored to normal by irradiation or by the administration of vitamin D.

Kramer, Casparis and Howland[50] found values for the inorganic phosphorus in the serum of the blood of rachitic infants to vary from 2.7 to 3.2 mgm. per cent. Under quartz lamp treatment, this increased gradually to a maximum of 6 mgm. per cent, the normal value. Hess and Lundagen[51] observed a seasonal variation in the level of the inorganic phosphates of the blood corresponding to and determined by the seasonal variations in the ultraviolet energy of the available solar spectrum.

By 1923, it was[52] reported that the mean serum calcium content of normal infants from two months to ten years of age varies between 10 and 12 mgm. per 100 cc. In twenty rachitic infants, it ranged from 7.9 to 10.4 mgm. with an average of about 9.2. Two children of three and eight years with irreducible

[46] Kramer, B., Casparis, H., and Howland, J., *Am. J. Diseases of Children*, **24**, 20 (1927); Levinsohn, S. A., *Ibid.*, **34**, 955 (1927).

[47] Gerstenberger H. J., and Hartman, J. I., *J. Am. Med. Assoc.*, **92**, 367 (1929).

[48] Gerstenberger, H. J., and Russell, G. R., *J. Am. Med. Assoc.*, **94**, 1049 (1930); Vollmer, H., *Klin., Wochschr*, **9**, 2300 (1930).

[49] Theiler, A., *Veterinary J.*, **90**, 159 (1934); *Chem. Abs.*, **28**, 5503 (1934).

[50] Kramer, B., Casparis, H., and Howland, J., *Am. J. Diseases of Children*, **24**, 20 (1922).

[51] Hess, A. F., and Lundagen, M. A., *J. Am. Med. Assoc.*, **79**, 2210 (1922).

[52] Lesné, E., deGennes, L., and Guillaumin, *Compt. rend.*, **177**, 291 (1923); *Chem. Abs.*, **17**, 3540 (1923); see also Kramer, B., and Boone, F. H., *Proc. Soc. Biol. Exptl. Med.*, **20**, 87 (1922).

rachitic deformations had normal or slightly greater amounts of calcium, 11.8 and 11.4 mg. respectively. The calcium content of the serum is not modified by the injection of calcium chloride, but is altered by ultraviolet rays. After eight daily irradiations of thirty minutes each at 1.2 meters from a 1200 c.p. carbon arc given ten infants the serum calcium was decidedly increased in seven and after 24 irradiations it was well up to the normal value in eight of the children. The two infants which failed to show an increase in the calcium had dark skins. Orr, Holt, Wilkins and Boone[53] also showed that infants with active rickets are unable to retain calcium and phosphorus even though these elements are present in adequate amounts in the diet and that ultraviolet rays cause these elements to be retained. They observed that after irradiation increased amounts of these elements are found in the urine, indicative of an increased absorption of these essential minerals from the intestine. They argued that defective intestinal absorption in rickets is the cause of the low serum calcium and phosphorus, and is the ultimate cause of the defective calcification of the bones. That calcification at the junction of the bones and cartilage could be promoted by irradiation also was demonstrated radiographically by Vignard, Mouriquand, Chassard and Bernheim.[54]

Clark[55] reported that the diffusible calcium of the serum, measured by dialysis in collodion sacks against physiological salt solution, may be increased by subjecting it to quartz mercury arc irradiations. The diffusible calcium in rabbit serum rose from 38 to 58% and in dog serum from 44 to 53%.

Hart, Steenbock and Elvehjem[56] induced experimentally negative calcium balances in mature lactating goats. Daily mercury arc irradiation changed these to positive and also appreciably increased the blood phosphorus. This was confirmed by Orr, Henderson and Magee,[57] who believed the results might be accounted for by a decreased elimination of calcium in the feces, the urinary excretion remaining practically constant. These results favored the view that irradiation induces an increased absorption of calcium from the intestines.

Schultzer[58] defines the Ca retention coefficient as the number of mg. retained per g. increase in body weight of rats during growth. The coefficient was 4.7 to 5.2 in young rats on a rachitic diet and with evident rickets. After irradiation, it was raised to 10. For phosphorus the values were 8.1 to 9.5 before and 15.7 after the cure of the rickets. Similar results also could be brought about by giving the rats cod-liver oil or, if the diet was deficient in phosphorus, by giving phosphates. A number of rachitic rats showed an average of 11.9 mgm. of calcium and 5.6 mgm. of phosphorus per 100 cc. of serum.[59]

In four ultraviolet-treated rats the serum calcium rose to 15.2 and the phosphorus to 8.6 mgm. per 100 cc. Normal rats on an ordinary diet failed to show this rise during irradiation. Burton[60] found in boys who had received some ultraviolet irradiation while on a diet high in calcium and phosphorus a high retention of these elements.

After daily exposures of gravid rats to sunlight, the lime of the fetuses increased 21.2

[53] Orr, W. J., Holt, L. E., Jr., Wilkins, L., and Boone, F. H., *Am. J. Diseases of Children*, **26**, 362 (1923). *Chem. Abs.*, **18**,

[54] Vignard, Mouriquand, Chassard, and Bernheim, *Lyon Medicale*, **132**, 1021 (1923); *Chem. Abs.*, **18**, 2382 (1924); Lesné, E., de Gennes, L., and Guillaumin, C., *Compt. rend.*, **177**, 291 (1923); *Chem. Abs.*, **17**, 3540 (1923); Howland, J., and Kramer, B., *Am. J. Diseases Children*, **22**, 105 (1921); *Chem. Abs.*, **17**, 413 (1923).

[55] Clark, J., *Am. J. Hyg.*, **3**, 481 (1923); *Chem. Abs.*, **18**, 2366 (1924).

[56] Hart, E. B., H. Steenbock and C. A. Elvehjem, *J. Biol. Chem.*, **62**, 117 (1924).

[57] Orr, J. B., Henderson, J. M., and Magee, H. E., *Biochem. J.*, **19**, 569 (1925).

[58] Schultzer, P., *Compt. rend. soc. biol.*, **93**, 1005 (1925); *Chem. Abs.*, **20**, 1655 (1926); *Biochem. Z.*, **188**, 409, 427 (1927); Mitchell, H. F., and Johnson, F., *Am. J. Physiol*, **72**, 143 (1925); Koch, E. M., and Cahan, M. H., *Am. J. Diseases of Children*, **34**, 187 (1927).

[59] Schultzer, P., *Compt. rend. soc. biol.*, **93**, 1008 (1925); *Chem. Abs.*, **20**, 1655 (1926).

[60] Burton, H. B., *J. Biol. Chem.*, **85**, 405 (1930).

per cent and the phosphate 19.2 per cent over that of the fetuses of non-irradiated rats. The phosphatase content, however, was not affected, according to Foa.[61]

Subsequent studies of the calcium and phosphorus in the blood serum in rickets have indicated that the disease may appear with either low phosphorus or low calcium or with both low in the serum. But if one is low and the other high there may be no rickets.[62] Kramer, Shear and Siegel[63] found the product of the calcium and phosphorus concentrations to be always thirty or less during rickets or during the cessation of calcification. When the product rises above forty, calcification may ensue no matter whether the healing is induced by cod-liver oil, phosphates, or artificially prepared vitamin D. There are, however, many recorded exceptions to this rule. Dietary ratios of calcium and phosphorus are important.[64] Many other papers deal with this topic, but are beyond the scope of this discussion.

At one time it was believed that an alteration of the pH of the substances in the intestinal tract was, in part at least, responsible for the failure of the proper absorption of calcium from the gut in rickets. Jephcott and Bacharach[65] stated that the alkalinity of the feces of animals on rachitic diets could be brought to the acid side of neutrality by irradiations or by administering cod-liver oil. It was assumed that determinations of the change in pH induced by various preparations containing vitamin D might be made the basis of an assay method for this vitamin. Wokes and Willimott[66] found that the method could not be applied to infants although they believed it gave satisfactory results in rats. Subsequent investigations, however, have shown the method unreliable.

The irradiation of nursing mothers whose breast milk had been failing was of general benefit in all of 53 cases in which the treatment was continued for some time, and was of aid in improving or retaining the milk supply in all but eleven of the cases.[67] Hess, Weinstock and Sherman[68] found that exposing a woman to the rays of a mercury-vapor quartz lamp every other day for a month produced antirachitic properties in her milk when fed to rats. During the control period the milk had no curative action. In similar experiments, Hirsch-Kauffmann and Wiener[69] found the quantity of the milk of irradiated mothers to be increased, although its chemical composition was unaltered except for a definite increase in vitamins C and D.

In children with various orthopedic disorders, exposure to all the sunshine available from May to August was not found to produce any symptoms characteristic of an overdose of vitamin D.[70]

Applications in Animal Husbandry

During the early development of irradiation therapy, attention was also devoted to the effects of ultraviolet light on farm animals. Hart, Steenbock and Jones[71] concluded that sunlight is a factor of economic importance in the production of pork in northern latitudes, and Maynard, Goldberg and Miller in New York[72]

[61] Foa, P., *Boll. soc. ital. biol. sper.*, **11**, 845 (1936); *Chem. Abs.*, **31**, 2622 (1937).

[62] See Hess, A. F., "Rickets, Osteomalacia and Tetany," Philadelphia, Lea and Febinger, 1929. Note also Orr, W. J., Holt, L. E., Jr., Wilkins, L., and Boone, F. H., *Am. J. Diseases of Children*, **26**, 362 (1923); Hess, A. F., Weinstock, M., Rivkin, H., and Gross, J., *J. Biol. Chem.*, **87**, 37 (1930); Hess, A. F., Lewis, J. M., and Rivkin, H., *J. Am. Med. Assoc.*, **94**, 1885 (1930).

[63] Kramer, B., Shear, M. J., and Siegel, J., *J. Biol. Chem.*, **91**, 271, 723 (1931).

[64] See also Shohl, A. T., and Bennett, H. B., *J. Biol. Chem.*, **76**, 633 (1928); Reed, C. I., Struck, H. C., and Steck, I. E., "Vitamin D" Chicago, Univ. of Chicago Press, 1939.

[65] Jephcott, H., and Bacharach, A. L., *Biochem. J.*, **20**, 1351 (1926).

[66] Wokes, F., and Willimott, S. G., *Pharm. J.*, **118**, 752, 793 (1927).

[67] Chisholm, C., and McKillop, M., *Lancet*, **II**, 227 (1927); *Chem. Abs.*, **22**, 2384 (1928).

[68] Hess, A. F., Weinstock, M., and Sherman, E., *Proc. Soc. Exptl. Biol. Med.*, **23**, 636 (1926).

[69] Hirsch-Kauffmann, H., and Wiener, C., *Klin. Wochschr.*, **8**, 984 (1929); *Chem. Abs.*, **23**, 4970 (1929).

[70] Dodds, E. C., Robertson, J. D., and Roche, H. J., *Arch. Diseases of Childhood*, **9**, 91 (1934); *Chem. Abs.*, **28**, 4459 (1934).

[71] Hart, E. B., Steenbock, H., and Jones, J. H., *J. Biol. Chem.*, **61**, 775 (1924).

[72] Maynard, L. A., Goldberg, S. A., and Miller, R. C., *J. Biol. Chem.*, **65**, 643 (1925).

found that sunlight improves the assimilation of calcium from a deficient diet and prevents the development of leg weakness in pigs. In a general discussion, Price [73] stated that besides an adequate amount of calcium and phosphorus in the diet of pigs it is essential for their health and growth that there also must be present either the antirachitic vitamin or exposure to sunlight. Henderson [74] found that the calcium and phosphorus retention of pigs receiving a poorly balanced diet, with P_2O_5:Ca:Mg as 3:1:1, was definitely increased by an irradiation of one hour per day for 24 days. No corresponding increase in body weight occurred, however.

It was believed by Bohstedt, Insko and Fargo [75] that for the health of the suckling pig dependence must be placed upon the antirachitic properties of the feed of the sow rather than upon the use of ultraviolet light, helpful as this may be. According to Isaachsen,[76] irradiation of sows in the last six weeks of gestation and of sows with litters did not improve the growth or condition of the pigs. He believed that pigs are more likely to suffer from disordered mineral metabolism as a result of a deficiency of minerals in the food or from an incorrect calcium-to-phosphorus ratio than from a lack of fat-soluble vitamins. Sinclair [77] found exposure to either sunlight or artificial sources, as well as cod-liver oil feeding, to promote growth in the pig, the response being inversely proportional to the calcium content of the basal ration. The addition of calcium to the ration aided greatly in the prevention of leg stiffness, a condition resembling rickets. Irradiation increased the level of the blood calcium.

Calves also require vitamin D. Calves fed on rations deficient in it show declining growth rates at the twelfth to the fifteenth week; and after the twenty-fifth week little growth occurs.[78] A decline in the level of inorganic phosphorus in the blood serum precedes the onset of stiffness. The percentage of total ash in the dry, fat-free bones is reduced from the normal of 60 to 63 per cent to 45 to over 50 per cent in the rachitic bones. The breaking strength of the bones also is lowered. Ultraviolet irradiation, sunlight or the feeding of liberal amounts of sun-cured hay protects the calves from the vitamin D deficiency.

Bechdel, Landsburg and Hill [79] also noted the abnormal bone development, swollen joints, and slight paralysis of the rear quarters and bowed back of vitamin D-deficient calves. Although cod-liver oil promoted growth and thriftiness slightly better than did ultraviolet light treatment, the latter produced a slightly superior grade of bone. Direct sunlight is not required if the ration contains sufficient vitamin D.[80]

The vitamin D requirement of dogs has been studied by Morgan.[81] Symptoms of rickets have been developed in a newly weaned cat fed 24 days on the Steenbock diet deficient in calcium and vitamin D.[82]

[73] Price, W. A., *Ind. Eng. Chem.*, **18**, 679 (1926).

[74] Henderson, J. M., *Biochem. J.*, **19**, 52 (1925); *Scottish J. Agr.*, **9**, 33 (1926); *Chem. Abs.*, **20**, 2523 (1926). See also Orr, J. B., Henderson, J. M., and Crichton, J. A., *Trans. Highland Agr. Soc. Scotland*, **38**, 88 (1926).

[75] Bohstedt, G., Insko, W. M., Jr., and Fargo, J. M., *Proc. Am. Soc. Animal Production*, 89 (1929); *Chem. Abs.*, **25**, 3695 (1931); see also Thalman, R. R., and Loeffel, W. J., *Proc. Am. Soc. Animal Production*, 83 (1928); *Chem. Abs.*, **25**, 3695 (1931).

[76] Isaachsen, H., *J. Agr. Sci.*, **22**, 460 (1932); *Chem. Abs.*, **27**, 1916 (1933).

[77] Sinclair, R. D., *Sci. Agr.*, **13**, 489 (1933); *Chem. Abs.*, **27**, 5787 (1933); Horn, V., *Biedermann's Zentralbl. B, Tierernähr.*, **6**, 203, 208 (1934); *Chem. Abs.*, **28**, 5855 (1934).

[78] Rupel, I. W., Bohstedt, G., and Hart, E. B., *Wisconsin Agr. Exp. Sta. Research Bull*, **115**, 40 pp. (1933); *Chem. Abs.*, **28**, 507 (1934).

[79] Bechdel, S. I., Landsburg, K. G., and Hill, O. J., *Pennsylvania Agr. Exp. Sta. Tech. Bull.*, **291**, 2 (1933); *Chem. Abs.*, **28**, 3028 (1934).

[80] Olson, T. M., *S. Dakota Agr. Exp. Sta., Bull.* **319**, 2 (1938); *Chem. Abs.*, **32**, 7970 (1938).

[81] Morgan, A. F., *North American Veterinarian*, **15**, No. 8, 24 (1934); *Chem. Abs.*, **29**, 201 (1935).

[82] Moody, C. A., *J. Home Econ.*, **28**, 696 (1936); *Chem. Abs.*, **31**, 436 (1937).

Irradiation and Poultry Culture. Because of the modern intensive methods of poultry culture, vitamin D deficiencies are quite common. Their remedy is a matter of considerable economic importance. Murray, Little and Bovie [83] found chicks exposed for only a few minutes each day to the rays of the mercury arc showed a more rapid formation of bone than did chicks exposed for many hours daily to direct sunlight.

Hughes, Titus and Moore [84] found that chicks fed on eggs from hens which were receiving direct sunlight developed normally, as shown by their general appearance and by the analysis of their blood and bones. Those fed on eggs from hens which received sunlight filtered through glass and supplemented by thirty minutes per day from a mercury arc developed some rickets. They were, however, in a better condition than those receiving eggs from hens which received no ultraviolet light other than that which came through a glass window. They believed thirty minutes of ultraviolet irradiation daily insufficient to enable hens to store sufficient antirachitic vitamin in their eggs to prevent entirely the development of rickets in chickens fed rations containing these eggs. Eggs of low antirachitic vitamin content do not have as high a hatchability as those with high vitamin content.[85]

Goodale [86] demonstrated that the amount of exposure to sunlight or ultraviolet light necessary for normal growth is but very small in the chick. Irradiations of one and ten minutes twice weekly at three feet from a mercury-vapor arc gave normal growth.[87]

DeVaney, Munsell and Titus [88] found that daily fifteen-minute irradiations with a carbon arc had approximately the same effect on vitamin D storage by hens as the addition of 1 per cent of cod-liver oil to the diet.

Hou [89] found rachitic chicks with intact preen glands to be cured when either the body, feet or head was irradiated. The degree of healing was greatest with the irradiation of the feet and least with the head. Rachitic chicks with the preen glands removed were not cured when the head was irradiated, but irradiation of the feet produced good healing. The substance which is activated when the feet are irradiated is apparently neither the preen gland material nor the circulating blood. Russell and Howard [90] delayed the onset of leg weakness in young chicks for about a week by an exposure to one day of winter sunlight through an ultraviolet transmitting material. There was also an indication of an effect on bone formation. A three-day exposure delayed the appearance of leg weakness about two and a half to three weeks and had a more enduring effect on bone formation.

Either cod-liver oil or ultraviolet irradiation of laying hens kept without access to direct sunlight or green feed increased the egg production, the thick-

[83] Murray, J. M., Little, C. C., and Bovie, W. T., *Maine Agr. Exp. Sta. Bull.* **320**, 141 (1924); *Chem. Abs.*, **19**, 3105 (1925).

[84] Hughes, J. S., Titus, R. W., and Moore, J. M., *Science*, **62**, 492 (1925); *Chem. Abs.*, **20**, 936 (1926); Hughes, J. S., Payne, L. F., Titus, R. W., and Moore, J. M., *J. Biol. Chem.*, **66**, 595 (1925).

[85] For the amounts of the vitamin required for the production of hatchable eggs, see Bethke, R. M., and Kennard, D. C., *Proc. Fourth World's Poultry Congress*, 342 (1930); *Chem. Abs.*, **25**, 4027 (1931). It has been suggested that sunlight may increase the hatchability of eggs by some mechanism other than vitamin D. Byerly, T. C., Titus, H. W., Ellis, N. R., and Nestler, R. B., *Poultry Sci.*, **16**, 322 (1937); *Chem. Abs.*, **31**, 8625 (1937).

[86] Goodale, H. D., *Am. J. Physiol.*, **79**, 44 (1926).

[87] Cf. also Price, W. A., *Science*, **63**, 1636 (1926); Russell, W. C., Massengale, O. N., and Howard, C. H., *J. Biol. Chem.*, **80**, 155 (1928); Maughan, G. H., and Dye, J. A., *J. Opt. Soc. Am.*, **20**, 279 (1930); *Proc. Soc. Exptl. Biol. Med.*, **28**, 106 (1930).

[88] De Vaney, G. M., Munsell, H. E., and Titus, H. W., *Poultry Sci.*, **12**, 215 (1933); *Chem. Abs.*, **27**, 5380 (1933).

[89] Hou, H.-C., *Chinese J. Physiol.*, **5**, 11 (1931); *Chem. Abs.*, **25**, 3037 (1931); see also Murphy, E. F., *J. Agr. Research*, **53**, 67 (1936); *Chem. Abs.*, **30**, 8319 (1936).

[90] Russell, W. C., and Howard, C. H., *J. Biol. Chem.*, **91**, 493 (1931).

ness of the egg shells and the general condition of the birds, according to Hendricks, Lee and Godfrey.[91] Each of these methods of supplementing the vitamin D also tended to increase the egg weight and the hatchability of the eggs. Cod-liver oil was superior to fifteen minutes of daily irradiation under the conditions employed. Dove[92] believed the chick superior to the rat for vitamin D research because it is more sensitive than the latter to a deficiency of that vitamin. Payne and Hughes[93] found direct sunshine somewhat more effective than ultraviolet irradiations from artificial sources in increasing the calcium content of the hen blood, of eggs and of newly hatched chicks. Maughan and Maughan[94] noted that ultraviolet irradiation of hens increases the vitamin D content of the egg yolk.[95]

Further studies on the vitamin D requirement of the chick have played an important part in the development of our knowledge of the chemistry of vitamin D and will be considered in the following chapter after the chemical changes underlying the formation of this substance have been discussed.

The Irradiation of Foodstuffs

During the years 1924 and 1925 it was discovered that, on analogy with the formation of antirachitic substances in the skin of irradiated animals, antirachitic potency is imparted to foodstuffs when these are submitted to the action of ultraviolet rays. Hume and Smith[96] were very near this important discovery when they reported that rats fed on a diet deficient in fat-soluble vitamins and kept in glass jars which had been exposed to quartz lamps for ten minutes every second day showed a prolongation of growth at a normal rate longer than that of controls kept in jars not so irradiated. Their work was conducted to determine whether the irradiation of the air played a part in the mechanism of the antirachitic resistance of irradiated animals. They showed definitely that ozone was not the effective agent, but overlooked the real cause of the beneficial effect they observed. Webster and Hill[97] showed that irradiated air could not have produced the beneficial results, and Hume and Smith later reported[98] that their results could be obtained only when the glass jars which were irradiated contained sawdust. When this was replaced by a piece of pine board, partial growth only resulted.[99] They had, however, missed their opportunity, for in the meantime Hess and Weinstock, as well as Steenbock and Black, had independently shown that certain foodstuffs can be rendered antirachitically active by irradiation.

On June 7, 1924, Hess reported the results of experiments conducted with Weinstock to the American Pediatrics Society[100] which indicated that vegetable

[91] Hendricks, W. A., Lee, A. R., Godfrey, A. B., *J. Agr. Research,* **43,** 517 (1931); *Chem. Abs.,* **26,** 1324 (1932).

[92] Dove, W. F., *Maine Agr. Exp. Sta. Bull.,* **360,** 172 (1931); *Chem. Abs.,* **27,** 1918 (1933).

[93] Payne, L. F., and Hughes, J. S., *Kansas Agr. Sta. Tech. Bull.,* **34,** 5 (1933); *Chem. Abs.,* **27,** 4277 (1933).

[94] Maughan, G. H., and Maughan, E., *Brit. J. Phys. Med.,* **7,** 137 (1932); *Chem. Abs.,* **27,** 5377 (1933).

[95] For calcium and phosphorus determinations in chicken blood, see Elvehjem, C. A. and Kline, B. E., *J. Biol. Chem.,* **103,** 733 (1933), and Higgins, G. M., Sheard, C., and Wilder, R. M., *Anat. Record,* **58,** 205 (1934).

[96] Hume, E. M., and Smith, H. H., *Biochem. J.,* **17,** 364 (1923).

[97] Webster, T. A., and Hill, L., *Proc. Physiol. Soc., J. Physiol,* **57,** LXXVIII (1923); *Chem. Abs.,* **18,** 278 (1924).

[98] Hume, E. M., and Smith, H. H., *Biochem. J.,* **18,** 1334 (1924).

[99] It was later shown by Rosenheim, O., and Webster, T. A., *Biochem. J.,* **20,** 1340 (1926) that a chloroform extract of irradiated sawdust has antirachitic activity.

[100] Hess, A. F., and Weinstock, M., *Abstracted in Am. J. Diseases of Children,* **28,** 256 (1924); **28,** 517 (1924). Also reported at a meeting of the New York Section, *American Chemical Society,* Jan. 9, 1925.

oils can be endowed with antirachitic properties on irradiation. Like Smith and Hume, they had started by attempting to activate air by ultraviolet light but obtained completely negative results. Their first favorable results were obtained when they irradiated cottonseed oil.[101]

Steenbock and Black[102] in a paper received for publication April 18, 1924, described an experiment in which a ration of hog millet 84, purified casein, 12, and salt, was irradiated for ten minutes at a distance of 23 inches from a Cooper-Hewitt quartz mercury-vapor lamp with a three-fourths inch arc operated at 120 volts. When fed, this ration produced a pronounced stimulation of the growth of rats. They also succeeded in imparting growth-promoting and bone-calcifying properties to olive oil and lard by this method. The activation took place when the ration was irradiated in an open dish or in a stoppered Pyrex or quartz flask filled with air or carbon dioxide, but it did not occur when the ration was irradiated in a brown glass bottle. The ash content of the bones of the rats receiving the irradiated ration was increased in percentage over that of rats receiving the same ration before irradiation. It was found also that the irradiation of fats, otherwise inactive in curing rickets, caused them to become active. Rations which ordinarily produced a wide rachitic metaphysis in the shaft bones of rats became antirachitic and promptly effected a rapid and complete healing of the lesion. Hess, in his complete paper, showed that although cottonseed and linseed oils could be activated by irradiation, this was not possible in the case of mineral oil, and also that ozonized water and hydrogen peroxide afforded no protection to rats on a deficient diet. Steenbock and Daniels[103] successfully produced antirachitic properties in a wide variety of foods, which included wheat, rolled oats, corn, hominy, meats, milk, egg-yolk and the vegetable oils. They suggested that it is the sterols in the foods which are altered during the irradiation process. Spinach was rendered antirachitic by Chick and Roscoe[104] and cabbage by Mellanby and Killick.[105] That the irradiation of cod-liver oil did not increase its antirachitic potency was demonstrated by Daniels and Brooks[106] and by Wyman, Holmes, Smith, Stockbarger and Pigott.[107]

Hume, Smith and Smedley-Maclean[108] succeeded in inducing antirachitic activity in yeast fat by irradiation and Daniels and Pyle and Brooks[109] showed that the use of milk irradiated a half hour at a distance of two feet from a mercury arc rendered it capable of bringing about prompt improvement in young rats. Gates and Grant[110] found that in normal rabbits the feeding of cod-liver oil or irradiated products did not produce changes in the relative

[101] Hess, A. F., and Weinstock, M., *J. Biol. Chem.,* **62,** 301 (1924). Goldblatt, H., and Soames, K. M., *Biochem. J.,* **17,** 446 (1923), had found that the livers of irradiated animals restored the growth of animals which had been inhibited by feeding certain diets.

[102] Steenbock, H., and Black, A., *J. Biol. Chem.,* **61,** 408 (1924); see also *Science,* **60,** 224 (1924); *J. Biol. Chem.,* **62,** 209 (1924).

[103] Steenbock, H., and Daniels, A. L., *J. Am. Med. Assoc.,* **84,** 1093 (1925).

[104] Chick, H., and Roscoe, M. H., *Biochem. J.,* **20,** 137 (1926).

[105] Mellanby, M., and Killick, E. M., *Proc. Physiol. Soc.,* **61,** xxiii (1926); *Chem. Abs.,* **20,** 3488 (1926). See also Drummond, J. C., Rosenheim, O., and Coward, K. H., *J. Soc. Chem. Ind.,* **44,** 135T (1925). For a clinical investigation of the curative value of irradiated food, see Mackay, H. M. M., and Shaw, H. F., *Lancet,* **I,** 82 (1926).

[106] Daniels, A. L., and Brooks, L. M., *Proc. Soc. Exptl. Biol. Med.,* **24,** 971 (1927).

[107] Wyman, E. T., Holmes, A. D., Smith, L. W., Stockbarger, D. C., and Pigott, M. G., *Boston Med. & Surg. J.,* **195,** 525 (1926); *Am. J. Diseases Children,* **34,** 753 (1927). See also Haffner, F., and Pulewka, P., *Klin. Wochschr.,* **5,** 2113 (1926).

[108] Hume, E. M., Smith, H. H., and Smedley-Maclean, I., *Biochem. J.,* **22,** 27 (1928).

[109] Daniels, A. L., Pyle, S. I., and Brooks, L. M., *Proc. Soc. Exptl. Biol. Med.,* **23,** 821 (1926); *Chem. Abs.,* **21,** 1831 (1927).

[110] Gates, F. L., and Grant, J. H. B., *Proc. Soc. Exptl. Biol. Med.,* **24,** 59 (1926).

weights of endocrine organs such as the external parathyroid and the hypophysis, although these organs are hypertrophied in rabbits after repeated exposure to the quartz mercury arc. It was shown by Goldblatt and Moritz[111] that irradiation does not increase the quantity of vitamin A in fats but forms only the antirachitic D.

Among the earlier suggestions regarding the mechanism by which irradiation may function was one which has been repeatedly discussed, but is no longer considered significant. Kugelmass and McQuarrie suggested that irradiation so alters the substances of foods as to make them capable during subsequent slow oxidation of emitting ultraviolet rays which affect a photographic plate.[112] As they themselves subsequently pointed out, many substances exhibit the property of affecting a photographic plate, the Russell effect; it bears little or no relation to the production of antirachitic activity and it is unnecessary to consider here the large number of papers by other workers who sought to explain the effect of irradiation upon foodstuffs in terms of this phenomenon.

For some time it was believed that the origin of the vitamin in the livers of fish could be attributed to their ingestion of other smaller fish which had in turn ingested diatoms in which the vitamin had been produced photochemically. There is, however, considerable evidence against this. Leigh-Clare was unable to detect the vitamin in the marine diatom *Nitzschia closterium*, and others[113] were unable to demonstrate it in phyto- and zoö-plankton from the ocean.[114] Bills[115] found the capelin, the chief food of the Newfoundland cod, a poor source. The enormous differences in the potencies of the liver oils from various species of fish suggest species differences in the ability to synthesize the vitamin and not merely in its storage. Attempts to produce more vitamin D in fish livers by irradiation of the fish have been unsuccessful.

Sunflower oil can be activated by irradiation by sunlight or artificial ultraviolet light.[116] The same is true of peanut oil.[117] The irradiated mycelium of Aspergillus oryzae, added to the diet of chicks to the extent of 0.05 per cent, makes them superior in health, appetite and growth to the controls.[118] Sun-dried alfalfa contains small amounts of vitamin D.[119] Clover hay made with exposure to sunlight showed considerable calcifying power, but clover hay made in the dark was inactive. If excessively weathered, it is reduced in activity as compared with hay less exposed to dew and rain, but it may be improved by subsequent mercury-arc irradiation.[120]

The potency of sun-cured hays is, however, too feeble to prevent the development of rickets in growing chicks fed ether extracts of the hays equivalent to a high concentration of the hay in the ration.[121] From 7 to 10 gms. of dry corn silage per kg. of feed cures and prevents rickets in yearling calves and supplies sufficient vitamin D for normal growth and reproduction in dairy cows.[122]

Völtz and Kirsch believed that grass germinated in darkness contains some of the antirachitic vitamin.[123]

[111] Goldblatt, H., and Moritz, A. A., *J. Biol. Chem.* **71,** 127 (1926).

[112] Kugelmass, I. N., and McQuarrie, I., *Science,* **60,** 272 (1924); **62,** 87 (1925); Drummond, J. C., and Coward, K. H., *J. Soc. Chem. Ind.,* **44,** 255 (1925).

[113] Leigh-Clare, J. L., *Biochem. J.,* **21,** 368 (1927); Drummond, J. C., and Gunther, E. R., *Nature,* **126,** 398 (1930).

[114] Belloc, G., Fabre, R., and Simonnet, H., *Compt. rend.,* **191,** 160 (1930).

[115] Bills, C. E., *J. Biol. Chem.,* **72,** 751 (1927).

[116] Markar'yan, E. A., *Proc. Sci. Inst. Vitamin Research, U.S.S.R.,* **1,** 207 (1936); *Chem. Abs.,* **31,** 1854 (1937).

[117] Rondoni, P., *Sperimentale,* **80,** 443 (1926); *Chem. Abs.,* **21,** 761 (1927).

[118] Yokoyama, K., and Takata, R., *J. Agr. Chem. Soc. Japan,* **12,** 909 (1936); *Chem. Abs.,* **31,** 1468 (1937).

[119] Scheunert, A., and Schieblich, M., *Biedermann's Zentr. B. Tierernährung,* **6,** 112 (1934); *Chem. Abs.,* **28,** 5102 (1934).

[120] Steenbock, H., Hart, E. B., Elvehjem, C. A., and Kletzien, S., *J. Biol. Chem.,* **66,** 425 (1925).

[121] See also Bechdel, S. I., Landsburg, K. G., and Hill, O. J., *Pa. Agr. Exp. Sta. Tech. Bull* **291,** (1933); *Chem. Abs.,* **28,** 2038 (1934).

[122] Bechtel, H. E., Huffman, C. F., Duncan, C. W., and Hoppert, C. A., *J. Dairy Sci.,* **19,** 359 (1936); *Chem. Abs.,* **30,** 5617 (1936).

[123] Völtz, W., and Kirsch, W., *Biochem. Z.,* **186,** 255 (1927).

Chapter 39

The Photochemistry of the Formation of Vitamin D

Early Observations Regarding the Precursor

Following the discovery of the ability of irradiation to render foodstuffs antirachitically active, there began an active search to determine which components of these materials are effectively altered during the irradiation. Such components as chlorophyll, hemoglobin, glycerol, starch, alkaloids and the phosphatides of egg-yolk were soon eliminated.[1] It was soon demonstrated that the vitamin is a component of only the unsaponifiable fraction of irradiated oils and that the chief components of the unsaponifiable portions of the oils, the sterols, have the property of being activated by irradiation.[2] This was shown in the case of the phytosterol prepared from cottonseed oil and of cholesterol isolated from brain tissue. Since it was known that the skin of animals contains much cholesterol, Hess suggested that when the animal is irradiated it is the cholesterol of the skin which is changed, or as it was then said, activated.[2a]

Steenbock and Black[3] were able to impart antirachitic activity to purified cholesterol by irradiation with either a mercury arc, a carbon arc or direct sunlight. They observed the significant fact that irradiation for prolonged periods destroyed the activity of natural cod-liver oil and also the activity artificially produced by shorter irradiations of vegetable oils, although in darkness the activity was maintained as long as ten months. They believed that old oils which had become acid could no longer be activated, although this was not held due to the acidity as such, since the addition of oleic acid to the oil did not interfere with the process of activation.

That the antirachitic properties of irradiated cholesterol, like those of cod-liver oil, can be destroyed by heating with butyronitrile was believed by Bills[4] to support, although not to prove, the identity of the irradiation product of cholesterol with the vitamin of cod-liver oil. That the rays which render cholesterol active are those which cure the animal in irradiation therapy was shown by Hess and Weinstock.[5] They also showed that the dihydroderivatives of cholesterol or of the phytosterol of wheat could not be made to acquire antirachitic activity by irradiation. This indicated unsaturation to be a necessary, but not a sufficient condition, determining the ability of a compound to function as a precursor of the vitamin.

[1] Hess, A. F., Weinstock, M., *J. Biol. Chem.,* **63,** 297 (1925); **62,** 301 (1924); Drummond, J. C., Coward, K. H., and Rosenheim, O., *J. Soc. Chem. Ind.,* **44,** 123T (1925). See also Dutcher, R. A., and Kruger, J. H., *J. Biol. Chem.,* **69,** 277 (1926). Waltner, K., *Magyar Orvosi Arch.,* **28,** 6, 13, 19 (1927); *Chem. Abs.* **21,** 1480 (1927), claimed to have "activated" tyrosine, but this was disproved by Kon, S. K., and Moore, T., *Biochem. J.,* **21,** 1368 (1927) and later by Waltner himself, *Magyar Orvosi Arch.,* **29,** 151 (1928); *Chem. Abs.,* **22,** 4155 (1928).

[2] Hess, A. F., Weinstock, M., and Hellman, F. D., *Proc. Soc. Exptl. Biol. Med.,* **22,** 76 (1924).

[2a] This term must not be confused with photochemical activation in the sense of excitation of a molecule to a higher energy level.

[3] Steenbock, H., and Black, A., *J. Biol. Chem.,* **64,** 263 (1925).

[4] Bills, C. E., *J. Biol. Chem.,* **66,** 451 (1925).

[5] Hess, A. F., and Weinstock, M., *J. Biol. Chem.,* **64,** 181 (1925).

Rosenheim[6] verified the activatability of cholesterol and, with Webster,[7] obtained a fraction of the irradiated material which protected against rickets when given in daily doses of but 0.01 mg.

Attempts were soon made to activate various derivatives of cholesterol and analogous compounds. Hottinger[8] found that the salts of the bile acids could not be rendered antirachitic by irradiation. Although he obtained no indications of growth-promoting power in irradiated solutions of cholesterol acetate or palmitate, Hottinger stated that cholesterol oleate can be made antirachitic and Bills and McDonald[9] found the same to be true of the acetate, isobutyrate and benzoate although not of cholesterol ethers. They established that the double bond of cholesterol must remain intact for the change to occur, although the alcohol group may be esterified. Schlutz, Ziegler and Morse[10] definitely eliminated the oxidation products of cholesterol as α- and β-cholesteryl oxides, hydroxycholesterol, and α-cholestantriol as either the vitamin or its precursor. They made the suggestion that the provitamin of cholesterol might have been, both in their own experiments and those of others, some difficultly removable impurity rather than cholesterol itself. Epicholesterol cannot be rendered antirachitic by irradiation.[11]

According to Hume and Smith,[12] the sterols obtained from the small Siak-illipe nut can be activated. Hess and Anderson[13] found that irradiation makes α-sitosterol strongly antirachitic, but does not affect the β- and γ-sitosterols.[14]

Von Euler, von Euler and Rydbom[15] found it possible to activate the sterols extracted from dried red blood cells.[16] They also observed the possibility of activating the phosphate and phosphite esters of sterols. Coprosterol, being an isomer of dihydrocholesterol and therefore lacking double bonds, cannot be activated.[17] The same is true of cerevisterol from yeast.[18]

Early Views as to the Change Involved. Certain features of the mechanism of the irradiation process were made clear even in this early phase of the investigations. No change in the elementary composition of cholesterol could be detected by Hess, Weinstock and Sherman[19] after an hour of irradiation. This was an essentially correct observation which did not receive sufficient credence, since it was thought that combustion methods might not detect a slight amount of change in the composition of the highly active, but unisolated product of the irradiation. Windaus,[20] however, made the suggestion that

[6] Rosenheim, O., *Lancet*, **I**, 1025 (1925); see also Kramer, B., Shear, M. J., and Shelling, D. H., *J. Biol. Chem.*, **71**, 213, 221 (1926).

[7] Rosenheim, O., and Webster, T. A., *Biochem. J.*, **20**, 537 (1926).

[8] Hottinger, A., *Z. Kinderheilk.*, **43**, 8 (1927); *Chem. Zentr.* **II**, 2036 (1928); *Chem. Abs.*, **21**, 3219 (1927).

[9] Bills, C. E., and McDonald, F. G., *J. Biol. Chem.*, **72**, 13 (1927).

[10] Schlutz, F. W., Ziegler, M. R., and Morse, M., *J. Biol. Chem.*, **73**, 209 (1927).

[11] Marker, R. E., Kamm, O., Oakwood, T. S., and Laucius, J. F., *J. Am. Chem. Soc.*, **58**, 1948 (1936).

[12] Hume, E. M., and Smith, H. H., *Biochem. J.*, **20**, 340 (1926).

[13] Hess, A. F., and Anderson, R. J., *J. Biol. Chem.*, **74**, 651 (1927).

[14] For the irradiation of anhydrous lanolin, see Bernhard, A., and Drekter, I. J., *J. Biol. Chem.*, **93**, 1 (1931); Töpelmann, H., and Schuknecht, W., *Z. Vitaminforschung*, **4**, 111 (1935); *Chem. Abs.*, **29**, 5596 (1935); Schieblich, M., and Pallaske, G., *Deut. Med. Wochschr.*, **61**, 957 (1935) Zurukzoglu, S., and Mündel, O., *Z. Vitaminforschung*, **6**, 125 (1937); *Chem. Abs.*, **31**, 5446 (1937).

[15] von Euler, H., von Euler, B., and Rydbom, M., *Arch. Med. Skand.*, **68**, 371 (1928); *Chem. Abs.*, **22**, 4591 (1927).

[16] Even cholesterol or lipins from the snail can acquire antirachitic properties, Mouriquand, G., and Leulier, A., *Compt. rend.*, **188**, 1701 (1929).

[17] Rosenheim, O., and Webster, T. A., *Biochem. J.*, **20**, 537 (1926).

[18] Honeywell, E. M., and Bills, C. E., *J. Biol. Chem.*, **99**, 71 (1932).

[19] Hess, A. F., Weinstock, M., and Sherman, E., *J. Biol. Chem.*, **66**, 145 (1925).

[20] Windaus, A., and Hess, A., *Nachr. Ges. Wiss. Göttingen, Math. Phys. Kl.*, 175 (1926); *Chem. Abs.*, **22**, 256 (1928).

the activation might involve a stereoisomerization to *allo*-cholesterol, a suggestion which proved incorrect. The melting point of a sample of cholesterol which melted sharply at 146°C. was altered[21] by irradiation so that it melted over a range of about 20°C. Some of its color reactions, notably the Whitby test, became negative.

Oxygen was not essential to the conversion, since Hess, Weinstock and Sherman[22] showed that it could be effected by irradiation under nitrogen. Contradictory reports by Tiede and Reyher in the case of milk[23] may have been due to their reliance upon odor and taste rather than an actual test of potency. Hess, Weinstock and Sherman[24] believed an active fraction from irradiated cholesterol to be soluble in liquid ammonia. Attempts by these authors to fractionate the altered material from unchanged cholesterol by recrystallization methods with alcohol as solvent[25] were unsuccessful; a gradual loss of the antirachitic activity occurred. Nitzescu, Popoviciu[26] and Denes-Goetz claimed to have attained some degree of concentration by such methods.

A method which proved extremely fruitful was introduced by Nelson and Steenbock.[27] It consisted in the precipitation of the unaltered cholesterol as a molecular compound with digitonin, a much used method in sterol chemistry. The antirachitic factor was found not to be precipitated by this reagent. The method is employed quantitatively for determining the extent to which the cholesterol has been altered during a given irradiation. The difference between the amount of sterol treated and that which can be recovered by digitonin precipitation represents the amount which has been photochemically altered. Cholesterol liberated from the digitonin precipitate was found to be capable of activation on renewed irradiation. Similar results were obtained by Hess, Weinstock and Sherman.[28]

On prolonged irradiation the antirachitic activity first produced is destroyed. This process is irreversible.[29] Prolonged irradiation of cod-liver oil deprives it of its antirachitic vitamin. This, Adam[30] suggested, might be due to an oxidative cleavage with the production of an acid, the iodine number being inversely proportional to the time of irradiation. Hottinger[31] also observed that the antirachitic material is irreversibly destroyed by heating it at 150 to 200°C. and partially so at 100 to 120°C. Bills and Brickwedde[32] found that greater activity could be attained by irradiating cholesterol at liquid air temperature than at room temperature. Cholesterol solutions in oils irradiated in oxygen

[21] Von Euler, H., Myrbäck, K., and Karlsson, S., *Z. physiol. Chem.*, **157**, 263 (1926).

[22] Hess, A. F., Weinstock, M., and Sherman, E., *J. Biol. Chem.*, **66**, 145 (1925).

[23] Tiede, E., and Reyher, P., *Naturwiss.*, **14**, 741 (1926).

[24] Hess, A. F., Weinstock, M., and Sherman, E., *J. Biol. Chem.*, **70**, 123 (1926).

[25] Hess, A. F., Weinstock, M., and Sherman, E., *J. Biol. Chem.*, **66**, 145 (1925).

[26] Nitzescu, I. I., Popoviciu, G., and Denes-Goetz, J., *Bull. soc. chim. biol.*, **9**, 126 (1927); *Brit. Chem. Abs.*, **1927A**, 487.

[27] Nelson, E. M., and Steenbock, H., *J. Biol. Chem.*, **64**, 299 (1925).

[28] Hess, A. F., Weinstock, M., and Sherman, E., *J. Biol. Chem.*, **70**, 123 (1926). See also Nitzescu, I. I., Popoviciu, G., and Denes-Goetz, J., *Bull. soc. chim. biol.*, **9**, 126 (1927); *Chem. Abs.*, **21**, 487 (1927). Occasional inaccurate statements imply that the vitamin may be precipitated by digitonin, *e.g.*, Beumer, H., *Klin. Wochschr.*, **5**, 1952 (1926). Thus Hess, A. F., and Sherman, E., *Proc. Soc. Exptl. Biol. Med.*, **23**, 169 (1925) believed irradiated cholesterol to delay the hemolytic action of digitonin by binding it more readily than does cholesterol. See also Hottinger, A., *Z. Kinderheilk.*, **43**, 8 (1927); *Chem. Zentr.* **II**, 2036 (1928); *Chem. Abs.*, **21**, 3219 (1927).

[29] Hess, A. F., Weinstock, M., and Sherman, E., *J. Biol. Chem.*, **66**, 145 (1925).

[30] Adam, A., *Klin. Wochschr.*, **5**, 1648 (1926); *Chem. Abs.*, **21**, 119 (1927).

[31] Hottinger, A., *Z. Kinderheilk.*, **43**, 8 (1927); *Chem. Zentr.* **II**, 2036 (1928); *Chem. Abs.*, **21**, 3219 (1927).

[32] Bills, C. E., and Brickwedde, F. G., *Nature*, **121**, 452 (1928).

exhibit a change in dielectric constant, according to Ellinger.[33] This is attributed to an oxidation process rather than to the formation of the antirachitic substance since it does not occur during irradiations in the absence of air, under which conditions the vitamin can be formed. Bills and McDonald[34] succeeded in obtaining a slight degree of activation of cholesterol without irradiation by treatment with a certain fuller's earth called floridin.

Ultraviolet Absorption Studies and Ergosterol as a Provitamin

Studies of the alterations of the absorption spectra of sterols during the formation of vitamin D directed attention to ergosterol, a difficultly removable contaminant of cholesterol as the precursor.[35] Von Euler[36] had found that the ability of various oils to be converted into the vitamin did not parallel their cholesterol content. It has subsequently been demonstrated that the important contaminant of cholesterol is not predominantly ergosterol, but rather the spectroscopically indistinguishable 7-dehydrocholesterol.

It was first shown by Hess and Weinstock[37] that although the spectrum of dihydrocholesterol, which cannot be activated, remained unaltered during its irradiation, that of cholesterol underwent a series of changes. Irradiation for about an hour decreased the absorption by the cholesterol, but prolonged irradiation had the opposite effect. After 17 hours, the material had become somewhat yellow in color and melted at a lower temperature, and after 30 hours it was opaque to both the ultraviolet and blue rays. Schlutz and Morse[38] made the premature suggestion that the early disappearance of the absorption bands of cholesterol might be taken as an index of the potency attained, thus avoiding the necessity of prolonged animal experiments. Subsequent developments, however, showed the spectrographic changes to be extremely complicated.

Soon, however, other workers in three laboratories showed that some of the absorption bands exhibited by cholesterol were really due to an impurity. Rosenheim and Webster[39] showed that when the cholesterol had been purified through the dibromide it could no longer be made antirachitic by irradiation. The usual methods of purification, however, did not remove the impurity which is capable of producing the vitamin on irradiation. This is an instance of a peculiar difficulty inherent in the chemistry of the sterols in general. These substances have a tendency to form loose associations with each other, with their derivatives, and with other compounds, notably the bile acids, which renders it very difficult to obtain pure compounds by even many recrystallizations. Heilbron, Morton and Kamm[40] by fractional crystallization of cholesterol from ethyl acetate, concentrated a substance in the least soluble fraction which had three well-defined absorption bands at 2930, 2800 and 2690A. These

[33] Ellinger, P., *Arch. exptl. Path. Pharmakol.*, **122**, 238 (1927); see also Remezov, I., *Biochem. Z.*, **248**, 256 (1932); **250**, 560 (1932); Yeremenkow, N. P., *Arch. sci. biol. (U.S.S.R.)*, 37, 509, 542 (1935); *Chem. Abs.*, **30**, 6021, 7041 (1936).

[34] Bills, C. E., and McDonald, F. G., *J. Biol. Chem.*, **68**, 821 (1926); **72**, 1 (1927); see also Yoder, L., *Science*, **80**, 385 (1934).

[35] This work has been reviewed by Loofbourow, J. R., *Bull. Basic. Sci. Research*, **3**, 101, 201 (1931); **4**, 59 (1932).

[36] von Euler, H., *Arch. Kemi Mineral Geol.*, **9**, 28 (1925).

[37] Hess, A. F., and Weinstock, M., *J. Biol. Chem.*, **64**, 181, 193 (1925); Hess, A. F., Weinstock, M., and Helman, F. D., *Proc. Soc. Exptl. Biol. Med.*, **22**, 227 (1924-5).

[38] Schlutz, F. W., and Morse, M., *Am. J. Diseases of Children*, **30**, 199 (1925); Schlutz, F. W., and Ziegler, M. R., *J. Biol. Chem.*, **69**, 415 (1926).

[39] Rosenheim, O., and Webster, T. A., *J. Soc. Chem. Ind.*, **45**, 932 (1926); *Biochem. J.*, **20**, 537 (1926).

[40] Heilbron, I., Morton, R. A., and Kamm, E. D., *J. Soc. Chem. Ind.*, **45**, 932 (1926); *Biochem. J.*, **21**, 78 (1927).

disappeared when the substance was irradiated, either in the solid state or in solution in alcohol or ether. At Göttingen, Pohl[41] found a sample of cholesterol which exhibited an inflection at about 2700A, a peak at about 2800 and an inflection at about 2900A to be altered by irradiation by a magnesium spark in such a way as to increase the transmission between 2500 and 3100A. As great a change could be produced in ten minutes with a magnesium spark with strong lines between 2800 and 2850A as could be obtained with the unfiltered mercury arc in an hour. By subtraction of the absorption curve obtained after an irradiation of twenty minutes from the original absorption curve of the sample there was obtained an absorption curve of the material which had been altered by the irradiation. This curve was subsequently shown to correspond to the absorption curve of ergosterol.[42] The decrease in extinction values at 2800A, indicated that, had the original absorption band truly belonged to cholesterol, about half of the sample must have been altered during the irradiation. Actually, however, at least 99.5 per cent of the original cholesterol could be recovered unchanged after such a treatment. The absorption which is altered during the irradiation must, therefore, be that of a contaminant. From the extinction values of ergosterol, Pohl concluded that his original cholesterol samples had been contaminated with this sterol to the extent of about one in 6000. Bills, Honeywell and McNair[43] found the ergosterol bands shown by samples of cholesterol could be made to disappear by treatment with charcoal. The original samples had been contaminated to the extent of about 1.2 parts per thousand. The disappearance of the ergosterol bands of ordinary cholesterol and bromide-purified cholesterol to which ergosterol had been added, during treatment with a permanganate solution was so similar as to afford further evidence that ergosterol is at least a contaminant of cholesterol. Rosenheim and Webster[44] estimated the intensity of the absorption by ergosterol to be from 1500 to 2000 times that of brain cholesterol. By irradiating ergosterol itself rather than cholesterol they soon obtained far more potent preparations than those obtainable by the irradiation of cholesterol. Similar results have been reported for the case of the zymosterol of yeast.[45]

Ergosterol is a sterol first isolated by Tanret from ergot, a fungus on rye, a material which itself is said to have a definite antirachitic action on dogs.[46] It is also present in yeast, and is apparently present in both animal and plant cells as a contaminant of their respective sterols. Its occurrence in such vegetable oils as that of the peanut has been reported by Morton, Heilbron and Kamm[47] and it was detected in animal skin (pig) by Rosenheim and Webster.[48] The structures of cholesterol and ergosterol are given below. There remains one doubtful point in the latter. The formula given is that of Windaus, in which one double bond is placed in the C_7—C_8 position. Heilbron places it in the C_8—C_9 position. This would mean that the two double bonds in Ring B are not in conjugation. Against this Dimroth and Traut-

[41] Pohl, R., *Nachr. Ges. Wiss. Göttingen, Math. Physik. Kl.*, 142 (1926).

[42] Pohl, R., *Naturwiss.*, **15**, 433 (1927); *Nachr. Ges. Wiss. Göttingen, Math. Physik. Kl.*, 185 (1927).

[43] Bills, C. E., Honeywell, E. M., and McNair, W. A., *J. Biol. Chem.*, **76**, 251 (1928); Bills, C. E., *Ibid.*, **66**, 451 (1925).

[44] Rosenheim, O., and Webster, T. A., *Lancet*, **I**, 306 (1927); *Biochem. J.*, **21**, 381 (1927).

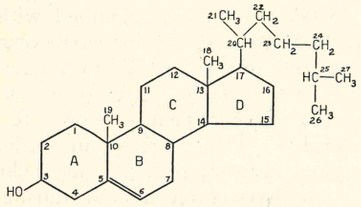
[45] Fabre, R., and Simonnet, H., *Compt. rend.*, **188**, 1312 (1929); Hume, E. M., Smith, H. H., and Smedley-MacLean, I., *J. Soc. Chem. Ind.*, **47**, 537 (1928); Hess, A. F., and Anderson, R. J., *J. Biol. Chem.*, **74**, 652 (1927).

[46] Mellanby, E., Surie, E., and Harrison, D. C., *Proc. Physiol. Soc., J. Physiol*, **65**, xxix (1928); *Chem. Abs.*, **23**, 1163 (1929); *Biochem. J.*, **23**, 710 (1929).

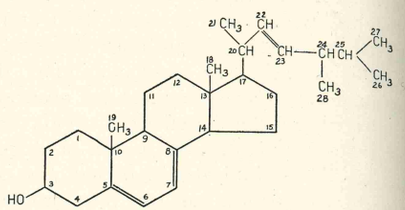
[47] Morton, R. A., Heilbron, I., and Kamm, E., *Biochem. J.*, **21**, 1279 (1927).

[48] Rosenheim, O., and Webster, T. A., *Biochem. J.*, **21**, 389 (1927).

mann[49] point out that such a structure would not be expected to give the characteristic absorption bands of ergosterol. They also show that ergostatriene, the unsaturated parent hydrocarbon of ergosterol, and 7-dehydrocholestene each have the same absorption spectrum as ergosterol, so that the hydroxyl group at position 3 does not influence the absorption.[50]



Cholesterol



Ergosterol

Various related compounds have been irradiated, with negative results.[51] Among these were Reindel's isoergosterol[52] and the fungisterol of ergot.[53] Positive results claimed by Windaus in the case of digitaligenin,[54] which like ergosterol contains three double bonds, could not be confirmed by Rosenheim and Webster. The absorption spectrum of ergosterol is given in Figure 152. During the irradiation of ergosterol, some of its color reactions suffer alteration. In the Meesemaecker reaction,[55] the addition of acetic anhydride and anhydrous zinc chloride to a chloroform solution of ergosterol produces a rose color which changes to a stable green. After irradiation of the ergosterol solution, however, only the green color results.[56]

Information Yielded by Studies of the Changes in Ultraviolet Absorption of Ergosterol During Irradiation.

Many of the earlier papers dealing with the conversion of ergosterol into an antirachitic product relied chiefly upon the evidence yielded by the changes in absorption for conclusions as to the nature of the processes occurring. The first object was to obtain from such studies a clear indication of the absorption spectrum of the antirachitic substance. The results were extremely confusing and led various workers successively to consider three different absorption maxima as characterizing the vitamin. It was at first believed to have a prominent band at about 2450A, but this was subsequently shown to characterize instead overirradiated solutions of but little antirachitic activity. Then it was thought that a band near 2800A, with greater extinction coefficients than that of ergosterol, might represent the vitamin; but this was later found in error due to the fact, since demonstrated in the laboratory of Windaus, that a number of reactions are involved in the formation of the vitamin, each

[49] Dimroth, K., and Trautmann, G., *Ber.*, **69B**, 669 (1936).
[50] See, however, Heilbron, I. M., *J. Soc. Chem. Ind.*, **55**, 129 (1936).
[51] Rosenheim, O., and Webster, T. A., *Biochem. J.*, **22**, 762 (1928).
[52] Reindel, F., Walter, E., and Rauch, H., *Annalen*, **452**, 34 (1927).
[53] Rosenheim, O., and Webster, T. A., *Lancet*, **II**, 622 (1927).
[54] Windaus, A., *Z. angew. Chem.*, **40**, 697 (1927); Windaus, A., and Holtz, F., *Nachr. Ges. Wiss. Göttingen, Math. Physik. Kl.*, 217 (1927); *Chem. Abs.*, **22**, 3910 (1928).
[55] Meesemaecker, R., *Compt. Rend.*, **190**, 216 (1930); *Brit. Chem. Abs.*, **A**, 477 (1930).
[56] See also Häussler, E. P., and Brauchli, E., *Helv. Chim. Acta.*, **12**, 187 (1929) for the effects of irradiation on the Tortelli and Jaffe reaction.

attended by absorption changes and in part occurring simultaneously. Finally, it has been established that the antirachitic material has an absorption band in the region of 2650A.

Pohl[57] found that irradiation of ergosterol solutions with a magnesium spark for 25 minutes caused a fading of the 2800A band of ergosterol resulting in a change in the absorption spectrum. By subtracting the original curve from that after irradiation, Pohl was led to conclude that the true absorption spectrum of the vitamin would be characterized by a band with a maximum at 2450A. Similar conclusions were reached independently by Morton, Heilbron and Kamm,[58] who observed that the band at 2470A disappeared on prolonged irradiation, just as vitamin D was known to be destroyed. Their assays, carried out by the fecal alkalinity method, were not sufficiently accurate to demonstrate that overirradiation had already occurred when the 2470A band appeared. Confirmation of the general course of the spectographic changes was afforded by Van Stolk, Dureuil and Heudebert.[59]

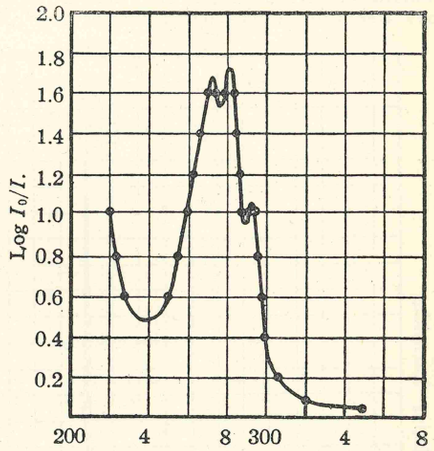


FIGURE 152.

Absorption of Ergosterol (Marshall and Knudson, *Journal American Chemical Society*).

The erroneous correlation of the band near 2470A with that of the vitamin led to the use of the appearance of this band as a criterion of suitable time and conditions of irradiation in commercial preparations of irradiated ergosterol introduced in Europe, and which were therefore actually overirradiated so that they contained toxic products. (See Chapter 38).

Bills, Honeywell and Cox[60] presented a curve for the potency of a 1 gm. per liter alcoholic solution of ergosterol after various times of irradiation in 2 cm. quartz cells directly in contact with the window of a water-cooled Kromayer lamp. Comparison of this curve with the absorption spectra obtained after various times of irradiation showed that the maximum potency had been attained and passed before the band near 2450A had become prominent, and that by the time it had reached its maximum, the potency had been largely destroyed. In a repetition of the work during which air was admitted into the cell, this band developed and faded more rapidly, but the activation curve was essentially the same as before. They believed that although oxidation might play a part in the destruction of the 2480A band, it was probably not concerned in the formation of the vitamin. They stated that the band at 2480 occurs also in the spectrum of an isoergosterol of Reindl, Walter and Rauch.[61] Rosenheim

[57] Pohl, R., *Naturwiss.*, **15**, 433 (1927).
[58] Morton, R. A., Heilbron, I. M., and Kamm, E. D., *J. Chem. Soc.*, 2000 (**1927**); see also Rosenheim, O., and Webster, T. A., *Lancet*, **II**, 622 (1927).
[59] Van Stolk, D., Dureuil, E., and Heudebert, *Compt. rend.*, **187**, 854 (1928); *Chem. Abs.*, **23**, 1166 (1929).
[60] Bills, C. E., Honeywell, E. M., and Cox, W. M., Jr., *J. Biol. Chem.*, **80**, 557 (1928).

and Webster also made it clear [62] that the 2450A band is characteristic of a degradation product and not of the vitamin. Tixier [63] concluded that the time when the absorption at 2537A is a maximum does not correspond to the time at which the antirachitic potency is greatest.

Smakula [64] continued the work of Pohl but used only very short irradiation periods [65] and excluded oxygen which he thought might alter some of the irradiation products. His observations eliminated the 2470A band as the vitamin absorption. He suggested that the true vitamin bands might be located near 2600 and 2900A.

Webster and Bourdillon [66] believed, as did Smakula, that during the early periods of irradiation, the absorption increases in a manner suggestive of the possibility that the vitamin has a band near 2800A. However, after the removal of unaltered ergosterol by digitonin precipitation, the absorption curve of the remaining solution showed less absorption than did that of ergosterol except in the region of wave-lengths longer than 3000A. This apparent decrease in absorption in the regions 2800 to 2900 they attributed to the simultaneous formation of some product without either absorption or antirachitic activity. Their belief that the vitamin absorbed at 2800A was founded in part upon the fact that a reirradiation of active preparations by filtered rays free from wave-lengths shorter than 2600A destroyed their antirachitic activity.

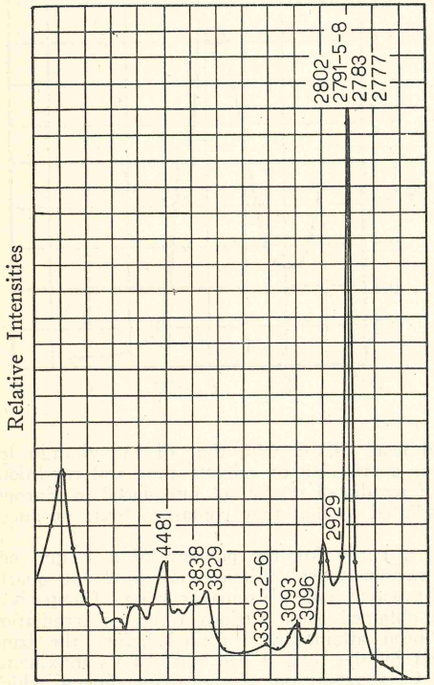


FIGURE 153.

Energy Distribution of Magnesium Spark (From Marshall and Knudson, *Journal of the American Chemical Society*).

[61] For further discussion of early work on the significance of this band, see Morrison, R. R., and Clark, L. H., *Brit. J. Radiology*, **2**, 307 (1929); *Chem. Abs.*, **23**, 5221 (1929); Fabre, R., and Simonnet, H., *Bull. soc. chim. biol.*, **10**, 1100 (1928); *Chem. Abs.*, **23**, 421 (1929); *Compt. rend. soc. biol.*, **99**, 193 (1928); *Chem. Abs.*, **22**, 3438 (1928); *Compt. rend.*, **188**, 424 (1929); *J. Pharm. chim.*, **9-10**, 331 (1929); Delaplace, R., and Rebière, G., *Compt. rend.*, **188**, 1169 (1929); Castille, A., and Ruppol, E., *Bull. Acad. Roy. Med. Belg.*, 799 (1929).

[62] Rosenheim, O., and Webster, T., *Biochem. J.*, **22**, 1223 (1928).

[63] Tixier, G., *Compt. rend.*, **188**, 206 (1929).

[64] Smakula, A., *Nachr. Ges. Wiss. Göttingen, Math. Physik. Kl.*, 49 (1928); *Chem. Abs.*, **23**, 1157 (1929).

[65] See also Knudson, A., and Moore, C. N., *J. Biol. Chem.*, **81**, 49 (1929).

[66] Webster, T. A., and Bourdillon, R. B., *J. Soc. Chem. Ind.*, **47**, 1060 (1928); *Biochem. J.*, **22**, 1223 (1928).

The importance of a band at 2650A was first emphasized by Reerink and van Wijk.[67] These workers studied separately the effects of irradiation by wave-lengths longer than about 2750A and by shorter wave-lengths. Their long wave-lengths were obtained by the use of either a mercury arc or a magnesium spark (Fig. 153), in either case filtered through a half cm. of a 10-per cent benzene solution. Hexane solutions of ergosterol were irradiated in quartz containers completely filled which had been cooled in solid carbon dioxide and evacuated by a high-vacuum pump, before sealing off. During the first fifteen minutes of irradiation there was an increased absorption throughout a large portion of the spectrum, later followed by a lessening of the absorption in the long wave-length region with but little change in the shorter wave-length region. The maximum at 2820A diminished from the beginning but that at 2715A increased at first. The nature of the changes in the absorption

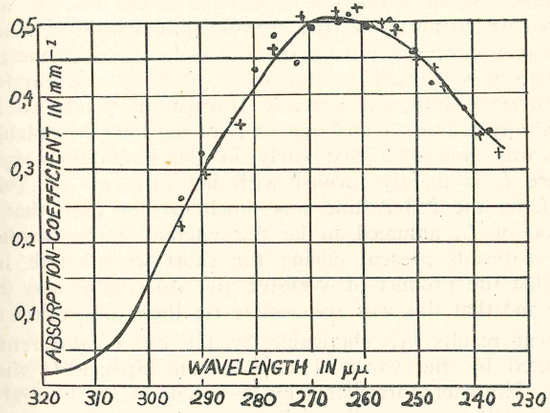


FIGURE 154. Absorption of Product L of Reerink and van Wijk *(Biochemical Journal)*.

curves suggested that several substances were formed successively. By the use of very short irradiation periods they found an early formed product to have the absorption curve obtained by the difference method of Pohl and Smakula indicated in Fig. 154. This was called product *L*. This absorption could be confirmed as that of the residue after removal of the unchanged ergosterol by digitonin precipitation if special precautions were taken to exclude oxygen. The single broad absorption band with its maximum near 2650A was attributed to the vitamin. There were some indications that it could be obtained as crystals at low temperatures. These authors believed that for irradiation periods up to about fifteen minutes, when 50 per cent of the ergosterol had been altered, practically all of the product consisted of the vitamin. After longer irradiation periods, 45 minutes to forty hours, larger quantities of secondary products with less absorption near 2700A appeared. After 25 hours of irradiation the ergosterol bands at 2800 and 2900A had practically disappeared and a broad band between 2400 and 2500A became prominent. Animal experiments by Everse

[67] Reerink, E. H., and van Wijk, A., *Biochem. J.*, **23**, 1294 (1929); *Proc. Acad. Sci. Amsterdam*, **32**, 845 (1929); *Chem. Abs.*, **24**, 1408 (1930); *Nederland, Maandschr. Geneesk.*, **17**, 1 (1930); *Chem. Abs.*, **24**, 4534 (1930); *Nature*, **122**, 648 (1928).

and van Niekerk[68] indicated the antirachitic activity to be closely correlated with the amount of this substance *L* calculated to be present from the spectrographic observations. Minimum daily doses of 100 γ of the most potent products (assumed from the degree of transformation of the ergosterol indicated by digitonin precipitation to be 50 per cent vitamin) cured rachitic rats in two weeks.

In their short wave-length experiments they employed a mercury argon source, operated to give chiefly an intense mercury resonance line at 2537A, with two filters, which transmitted most of the energy of this line. One, a 2-cm. column of saturated chlorine vapor at 6 atmospheres, absorbed the longer wave-lengths. The other, a 0.5-cm. column of 0.5-per cent aqueous potassium nitrate absorbed wave-lengths shorter than 2410A. Under these conditions, it seemed that from the start secondary reactions occurred. The general change seemed to be at first an increased absorption throughout the entire spectrum, followed by a gradual diminution culminating in practically complete transparency after 330 minutes. The ratios of the extinction coefficients of the 14-, 60- and 135-minute samples appeared independent of the wave-length within a wide range and indicated that these curves are representative of various concentrations of a substance *S*. This was marked by absorption at 2800A. Upon further irradiation, it was converted into a practically transparent product. From a comparison of the absorptions of *S* and that of *L* of the long wave-length irradiation experiments, it was concluded that early in the irradiations by short wave-lengths substance *L* is mainly formed with but little of *S*. But the rate of destruction of *L* by the 2537A line was much greater than that of *S* so that the concentration of *L*, assumed to be the vitamin, never made a high percentage of the materials present during the short wave-length irradiation. It was suggested that the product of Webster and Bourdillon may have contained the *S* substance and that this was responsible for their absorption results.

That divergent results are obtainable by the use of different wave-lengths was also indicated by the work of Griffith and Spence,[69] who employed a monochromator. Ergosterol irradiated by wave-lengths 2650A and shorter, when fed at a level of 0.01 mg. per day, failed to cure rats in two weeks but was effective in four weeks. Samples irradiated with rays in the range 2650 to 3130A cured in two weeks. Samples irradiated by still longer wave-lengths did not become antirachitic.

In subsequent work by Bourdillon, Fischmann and Jenkins,[70] it was shown that solutions of ergosterol of low concentration required shorter periods of irradiation to attain the maximum absorption at 2800A than those of higher concentrations. This is in agreement with the results of other photochemical changes outlined in the second section of this book. They also showed that when the radiations shorter than 2650A were filtered out the formation of the substance absorbing at 2800A was lessened, as had been shown by the Dutch workers, in the case of their substance *S*. They later agreed[71] that the substance with marked absorption between 2700 and 2800A is not the vitamin. They were able to obtain preparations of high potency but low absorption at 2800A. Lahousse and Gonnard[72] agreed in general with the results of Reerink and van Wijk. They found in the best products absorption at 2570 and probably

[68] See Everse, J. W. R., and van Niekerk, J., *Nederland Tijdschr. Geneesk.*, **75**, 1101 (1931); *Chem. Abs.*, **26**, 1010 (1932).

[69] Griffith, H. D., and Spence, K. C., *Brit. J. Actinotherapy*, **3**, 69 (1928).

[70] Bourdillon, R. B., Fischmann, C., and Jenkins, R., *Proc. Roy. Soc.*, **104B**, 561 (1929).

[71] Bourdillon, R. B., Jenkins, R., and Webster, T. A., *Nature*, **125**, 625 (1930).

[72] Lahousse and Gonnard, *J. phys. radium*, (6) **10**, 114S (1929).

also at 2690A but did not regard this product as the pure vitamin. It was also shown that even the substance *L* of Reerink and van Wijk was not a pure compound, two or more products being produced, probably in the same ratio in its formation. Some doubt was cast for a time upon the view that the vitamin has absorption at 2650A by the work of Ender,[73] who claimed that a very potent concentrate of the natural vitamin from tuna fish liver oil showed no selective absorption, a claim which has recently been shown erroneous.

Reerink and van Wijk[74] also observed that during the long-wave irradiation of ergosterol the optical rotation showed a linear dependence on the degree of transformation of the ergosterol. This they regarded as supporting the view that under their conditions but one product, the vitamin, is formed from ergosterol. This contrasted with the view of Askew, Bourdillon, Bruce, Jenkins and Webster,[75] who had obtained small amounts of a crystalline product with absorption maximum at 2680A, that the effect of long-wave irradiation is to produce simultaneously two substances, only one being the vitamin. Van Wijk, Reerink and Mörikofer[76] believed from absorption studies alone that the vitamin was more completely destroyed by prolonged exposure to sunlight than to the long-wave ultraviolet rays of the filtered mercury arc, a result they attributed to a difference in the distribution of energy from the two sources. Windaus[77] pointed out that long exposures to the magnesium spark are required to over-irradiate the vitamin, which he found to have a negative optical rotation and, from the observations of Holtz in his laboratory, to have an absorption maximum at about 2700A. It was also clear to Windaus that five or six irradiation products, all non-precipitable by digitonin, may form during the irradiation of ergosterol.[78] Haman and Steenbock[79] believe that the absorption at 2650A cannot be used as an accurate measure of the amount of the vitamin formed since the change is so complex.

Quantum Yields. During the period in which the emphasis was upon the spectrographic changes, little attempt was made to bring the principles of photochemistry to bear upon the problem. Some, such as Schlutz and Morse,[80] crudely conceived the irradiated material to be merely a storehouse of radiant energy which was later supposed to be reëmitted within the body, producing a sort of internal irradiation. Nevertheless, a few physical chemists made attempts (somewhat premature in view of the state of knowledge of the mechanism of the processes involved) to learn something of the amounts of energy required for the conversion of ergosterol or unpurified cholesterol into the vitamin. Fosbinder, Daniels and Steenbock[81] measured the ergs of the radiation 2650A required to produce a definite antirachitic potency in cholesterol and found the value to correspond to that in 3.2×10^{13} quanta. This was the energy required to produce a minimal threshold action. An attempt was made to calculate from this the least effective dose of the vitamin, the following assumptions being involved:

[73] Ender, F., *Z. Vitaminforschung*, **2**, 241 (1933); *Brit. Chem. Abs.*, **A**, 1340 (1933); *Chem. Abs.*, **28**, 4103 (1934).

[74] Reerink, E. H., and van Wijk, A., *Biochem. J.*, **25**, 1001 (1931).

[75] Askew, F. A., Bourdillon, R. B., Bruce, H. M., Jenkins, R. G. C., and Webster, T. A., *Proc. Roy. Soc.*, **107B**, 76, 91 (1930); Bourdillon, R. B., Jenkins, R. G. C., and Webster, T. A., *Nature*, **125**, 635 (1930).

[76] Van Wijk, A., Reerink, E. H., and Mörikofer, W., *Strahlentherapie*, **39**, 80 (1930-31); *Chem. Abs.*, **25**, 3034, 5692 (1931).

[77] Windaus, A., *Nachr. Ges. Wiss. Göttingen, Math. Physik Kl.*, 36 **(1930)**; *Chem. Abs.*, **25**, 132 (1931).

[78] See also Holtz, F., *Strahlentherapie*, **34**, 637 (1929).

[79] Haman, R. W., and Steenbock, H., *Wis. Agr. Exp. Sta. Bull.*, **430**, 136 (1935); *Chem. Abs.*, **30**, 3472 (1936); *cf.* Fuchs, L., *Pharm. Presse Wiss.-Prakt. Heft*, 93 **(1933)**; *Chem. Abs.*, **27**, 5478 (1933).

[80] Schlutz, F. W., and Morse, M., *Am. J. Diseases of Children*, **30**, 199 (1925).

[81] Fosbinder, R. J., Daniels, F., and Steenbock, H., *J. Am. Chem. Soc.*, **50**, 926 (1928).

(a) that the molecular weight of the vitamin is the same as that of cholesterol, (b) that the Einstein photochemical equivalence law applies and (c), although this was not recognized to be an assumption at the time, that no other simultaneous photochemical process occurs and that there is no loss of energy in any over-irradiation destroying the vitamin. The calculation indicated that the vitamin should be active in doses of 0.02γ. For the irradiation of ergosterol, the value was given as 0.06γ.[82] Shortly after this, Coward[83] found the best preparation then available to give a positive result in the line test, a biological assay, in daily doses of 0.02γ, a result which appeared a remarkable confirmation of the physicochemical predictions. By extending the results to three other wave-

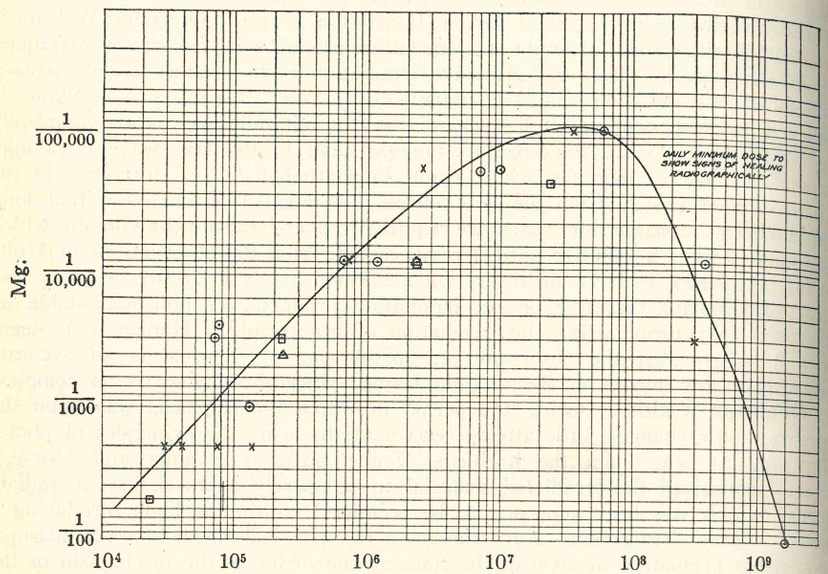


FIGURE 155. Amounts of Energy Required to Render Ergosterol Antirachitic (Marshall and Knudson, *Journal American Chemical Society*).

lengths, 2560, 2800 and 2930A, it was found that the results were independent of the wave-length, the same dosage being arrived at in each case. In these irradiations only very short exposures were employed to eliminate the possibility of a loss of energy in overirradiation. As a result of this work the quantum efficiencies were thought to be independent of the wave-length, and, from other experiments, of the state of the ergosterol, *e.g.*, as solid or in solution (and in the latter case of the concentration of the solution). At present, it would seem very unlikely that a quantum yield of unity logically could have been assumed for photochemical reactions of such complexity occurring in condensed phases and, indeed, Kon himself has stated that the process is probably one with a low quantum yield. An approximation of the quantum yields actually

[82] Kon, S. K., Daniels, F., and Steenbock, H., *J. Am. Chem. Soc.*, **50**, 2973 (1928).
[83] Coward, K. H., *Biochem. J.*, **22**, 1221 (1928).

obtained in these experiments is to be obtained by dividing the minimal dose (probably 0.03γ) of the more recent crystalline D_2 of Windaus and others by the calculated doses of Daniels (0.06γ). This gives a quantum yield of 0.5, still a remarkable agreement in view of the many assumptions involved. This work was extended by Marshall and Knudson[84] who plotted on log-log paper the minimum daily doses required to cure rats in three weeks which could be imparted to 0.3 mg. samples of ergosterol when irradiated by different amounts of energy at given wave-lengths. (See Figure 155). It was found that during the initial stages of irradiation the amount of the vitamin formed was directly proportional to the energy absorbed, since the minimum dose varied inversely with the ergs absorbed. For longer periods of irradiation, this relation failed, the net amount of the vitamin formed being smaller at each succeeding period until a stage was reached in which prolonged irradiation led to a loss in the vitamin previously produced. Thus these experiments yielded an independent confirmation of the results of spectrographic determinations. They calculated quantum yields of 0.3 to 0.2, based upon the potencies of the best preparations then available, those of Bourdillon and Webster. That this is greater than that of the D_2 mentioned in connection with the results of Daniels may account for the somewhat lower quantum yields of Marshall and Knudson. In two instances in which prolonged irradiations were made, the results with the 2536 and 2800A lines appeared to be identical. This result is hard to reconcile with the observations of Reerink and van Wijk.

Other Features of the Irradiation Changes

During this period a number of other observations tended to throw some light on the influence of various factors on the irradiation process. The discovery that the irradiation could be effected successfully at −183°C., a temperature at which most bimolecular reactions are markedly inhibited, suggested the likelihood that the reaction is a monomolecular process, probably an isomerization.[85] The process is markedly affected by the choice of solvent.[86] In ether, the maximum potency is about five times that which can be attained in alcohol. The maximum is reached in 27 minutes in alcohol but only after four hours in ether. The vitamin is destroyed much more slowly by overirradiation in ether. Cyclohexane as solvent is intermediate between alcohol and ether. The vitamin can be destroyed by x-rays.[87]

During the early studies attempts were made to render unpurified cholesterol antirachitic by the action of x-rays. Hess and Weinstock[88] were unable in this way to alter its absorption spectrum, but Roffo and Correa[89] found that it was thereby rendered nonprecipitable by digitonin. Reinhard and Buchwald[90] found the absorption to be shifted to longer wave-lengths by x-rays or γ-rays, although the change in optical rotation was but slight. No antirachitic potency was acquired, according to Stenstrom, Lohmann and Hillstrom.[91]

Knudson[92] found commercial cholesterol could be rendered antirachitic by the

[84] Marshall, A. L., and Knudson, A., *J. Am. Chem. Soc.*, **52**, 2304 (1930).
[85] Bills, C. E., and Brickwedde, F. G., *Nature*, **121**, 452 (1928).
[86] Bills, C. E., Honeywell, E. M., and Cox, W. M., Jr., *J. Biol. Chem.*, **92**, 601 (1931).
[87] Morrison, R. R., Peacock, P. R., and Wright, S., *Biochem. J.*, **22**, 1138 (1928); Sumi, M., *Bull. Inst. Phys. Chem. Research, (Tokyo)* **8**, 640 (1929); *Chem. Abs.*, **25**, 1875 (1931).
[88] Hess, A. F., and Weinstock, M., *J. Biol. Chem.*, **64**, 181 (1925).
[89] Roffo, A. H., and Correa, L. M., *Boll. Inst. Med. Exptl., No. 5* (1925); *Brit. Chem. Abs.*, A, 523 (1929).
[90] Reinhard, M. C., and Buchwald, K. W., *J. Biol. Chem.*, **73**, 383 (1927).
[91] Stenstrom, W., Lohmann, A., and Hillstrom, H. T., *Proc. Soc. Exptl. Biol. Med.*, **25**, 817 (1928).
[92] Knudson, A., *Science*, **66**, 176 (1927); Knudson, A., and Coolidge, W. D., *Proc. Soc. Exptl. Biol. Med.*, **24**, 366 (1927).

action of cathode rays. Hieger believed that[93] cholesterol could be made activatable by x-rays only in the presence of a chlorine-containing solvent.

Ergosterol can be rendered active by cathode rays, but the activity attainable is only 0.04 that attainable by the use of ultraviolet rays.[94] That soft x-rays may be employed for the formation of the vitamin has been observed by Delaplace and Rebière[95] and by Loofbourow and Shelow.[96] The glow discharge has been successfully employed by Askew, Bourdillon and Webster.[97] The claim of Takamiya[98] that ozone is able to effect the production of the vitamin is apparently incorrect in view of the work to be described in a subsequent section which shows that ozone would completely destroy features of molecular structure upon which the vitamin action depends.

Even before the isolation of crystalline irradiation products, it appeared likely that the change involved in the production of the vitamin is one of isomerization. Early suggestions of a correlation between the peroxide content of antirachitic products and their potency[99] did not prove significant. That oxygen is not essential to the occurrence of the desired change in ergosterol is apparent from the many investigations in which it was excluded without affecting the process.[100] Nevertheless, it was possible before the structural formula of the sterols was as well understood as at present, to conceive of a secondary alcohol group being converted into a ketone by a migration of hydrogen atoms to some double bond.[101] Heilbron, Morton and Sexton[102] tended to favor a ketone structure for the vitamin, particularly because of the results of studies of the monomolecular spreading on water of films[103] of the irradiation products in comparison with the types of spreading exhibited by various sterol derivatives. However, many arguments were quickly marshalled against this possibility. In the first place, since ergosteryl acetate can acquire vitamin properties, it is unlikely that the hydroxyl groups can be affected.[104] Infrared absorption studies[105] indicated the persistence of the alcohol group and the non-appearance of a ketone group during the irradiation, except possibly in over-irradiated products. This was in agreement with the conclusions of Windaus and Linsert[106] from chemical evidence. It was stated that the optical activity changes from about $-100°$ to $+15°$ in 45 hours, but that the molecular weight remains unchanged and a free hydroxyl group remains as shown by the action of methyl magnesium iodide. Hydrogenations and perbenzoic acid titrations of the best products then available appeared to indicate that the number of double bonds remains unaltered. (This was later shown to have been in error.) This stimulated a number of

[93] Hieger, I., *Biochem. J.*, **21**, 407 (1927).

[94] Knudson, A., and Moore, C. N., *J. Biol. Chem.*, **81**, 49 (1929); see also Hoffman, R. M., and Daniels, F., *J. Biol. Chem.*, **115**, 119 (1936).

[95] Delaplace, R., and Rebière, G., *Compt. rend.*, **188**, 1169 (1929).

[96] Loofbourow, J. R., and Shelow, E., *Bull. Basic Sci. Research*, **3**, 47 (1931).

[97] Askew, F. A., Bourdillon, R. B., and Webster, T. A., *Biochem. J.*, **26**, 814 (1932).

[98] Takamiya, E., *Bull. Agr. Chem. Soc. Japan*, **5**, 72 (1929); *Chem. Abs.*, **25**, 536 (1931); *J. Dept. Agr. Kyushu Imp. Univ.*, **3**, 1 (1930); *Chem. Abs.*, **25**, 1877 (1931).

[99] Yoder, L., *J. Biol. Chem.*, **70**, 297 (1926); Schimkus, B., *Arch. Exptl. Path. Pharmakol.*, **121**, 230 (1927); *Chem. Abs.*, **21**, 2335 (1927); Rousseau, E., *Compt. rend. soc. biol.*, **99**, 1844 (1928).

[100] See Beard, H. H., Burke, R. E., Thompson, H. E., and Goldblatt, H., *J. Biol. Chem.*, **96**, 307 (1932).

[101] See Windaus, A., and Linsert, O., [*Annalen*, **465**, 148 (1928)] for an early discussion of the chemical possibilities.

[102] Heilbron, I. M., Morton, R. A., and Sexton, W. A., *J. Chem. Soc.*, 47 (1928); Sexton, W. A., *Biochem. J.*, **22**, 1133 (1928).

[103] Rosenheim, O., and Adam, N. K., *Proc. Roy. Soc.*, **105B**, 422 (1929); Steigmann, A., [*Kolloid Z.*, **45**, 165 (1928); *Chem. Abs.*, **22**, 3432 (1928)] favored a ketone structure because of a color test.

[104] Heilbron, I. M., *Brit. J. Actinotherapy*, **2**, 210 (1928).

[105] Shelow, E., *Bull. Basic Sci. Res.*, **3**, 175 (1931); see also Hirsch, W., and Kellner, L., *Klin. Wochschr.*, **10**, 171 (1931); *Chem. Abs.*, **25**, 2173 (1931); *Biochem. Z.*, **235**, 162 (1931).

[106] Windaus, A., and Linsert, O., *Annalen*, **465**, 148 (1928); Windaus, A., Westphal, K., von Werder, F., and Rygh, O., *Nachr. Ges. Wiss. Göttingen, Math. Physik Kl.*, 45 (1920); *Chem. Abs.*, **24**, 4799 (1930); Windaus, A., *Nachr. Ges. wiss. Göttingen, Math. Physik Kl.* 36 (1930).

investigations regarding the possible potency or activatability of the various chemically prepared isomers of ergosterol in which the positions of the double bonds are shifted, as well as that of the stereoisomers.[107]

Isolation of Crystalline Irradiation Products

Attention was diverted to the study of crystalline irradiation products which were isolated about 1930. There were a few earlier observations. Jendrassik and Keményffi[108] claimed the isolation of a crystalline substance effective in a daily dose of 0.01γ. This may be doubted since the product was said to exhibit no ultraviolet absorption spectrum and since the activity claimed exceeds that of the well-characterized products later obtained by others.* The first definitely characterized crystals, isolated by Windaus, Gaede, Köser and Stein,[109] proved to be biologically inactive as a result of over irradiation (50 hours). They could be separated into two fractions by fractional crystallization of the allophanate from benzene. As an indication of the excessive irradiation employed, they were called suprasterols I and II. Neither showed absorption of wave-lengths longer than 2500A. They were not precipitated by digitonin and were not mutually interconvertible. Suprasterol I melted at 104°C. and II at 110°C. They appeared to be triply unsaturated monohydric alcohols.

Active crystals were obtained shortly after this by Askew, Bourdillon, Bruce, Jenkins and Webster.[110] Ergosterol in ether solution was irradiated by a mercury-vapor lamp while flowing through a quartz tube at such a rate that about 40 per cent of the ergosterol was altered. After removal of the unchanged sterol by digitonin precipitation, the solution was evaporated *in vacuo* to a dry resin. By distillation at pressures between 0.002 and 0.01 mm. there were obtained distillates which, on solution in alcohol with water added formed just opalescent liquids. These mixtures, on slow evaporation in a vacuum desiccator, gave crystals melting 113-115°C. The ultraviolet absorption of these crystals agreed with that of the substance *L* of Reerink and van Wijk and in several samples the absorption paralleled the biological activity. The crystals were at first thought to be a mixture of two or more very similar substances (only one of which might be the vitamin), or else mixtures of antirachitic substances of different degrees of potency.

It was shown that a product prepared by irradiation with longer wave-lengths suffered a change on subsequent irradiation by shorter wave-lengths (2100-2800A), the absorption increasing at 2800A and the antirachitic value falling. On the other hand, irradiation by long wave-lengths for fifteen minutes had but little effect on the antirachitic potency. It was suggested, from closer analysis of the results, that the inactive substance absorbing at 2800A is produced during the re-irradiation of the long wave-length product by short wave-lengths, not from the vitamin but from some other substance present, to an extent which depends

[107] Bills, C. E., and Cox, W. M., Jr., *J. Biol. Chem.*, **84**, 455 (1929); Bills, C. E., Cox, W. M., Jr., and Steel, G. E., *Ibid.*, **84**, 655 (1929); MacCorquodale, D. W., Steenbock, H., and Adkins, H., *J. Am. Chem. Soc.*, **52**, 2512 (1930); Hart, M. C., and Heyl, F. W., *Ibid.*, **52**, 2013 (1930); Emerson, H., and Heyl, F. W., *Ibid.*, **52**, 2015 (1930); Hart, M. C., Speer, J. H., and Heyl, F. W., *Ibid.*, **52**, 2016 (1930); Heilbron, I. M., Johnstone, F., and Spring, F. S., *J. Chem. Soc.*, 2248 (1929); Windaus, A., and Auhagen, E., *Annalen*, **472**, 185 (1929); Windaus, A., Dithmar, K., Murke, H., and Suckfüll, E., *Annalen*, **488**, 91 (1931); Cox, W. M., Jr., and Bills, C. E., *J. Biol. Chem.*, **88**, 709 (1930); Natelson, S., Sobel, A. E., and Kramer, B., *Ibid.*, **105**, 761 (1934); Natelson, S., and Sobel, A. E., *Ibid.*, **109**, 687 (1935).

[108] Jendrassik, A., and Keményffi, A. G., *Biochem. Z.*, **216**, 238 (1929).

* Reerink and van Wijk, it may be recalled, stated that they had evidence of crystals at low temperatures in their products.

[109] Windaus, A., Gaede, J., Köser, J., and Stein, G., *Annalen*, **483**, 17 (1930).

[110] Askew, F. A., Bourdillon, R. B., Bruce, H. M., Jenkins, R. G. C., and Webster, T. A., *Proc. Roy. Soc.*, **107**, 76, 91 (1930).

upon the conditions used in the first irradiation. They did not believe this to be a precursor of the vitamin but some other substance formed simultaneously with it. The simultaneous production of two products, one of which is inactive, would prevent the concentration of the vitamin produced by irradiation from ever reaching 100 per cent. Within a year they had improved the technique[111] to an extent that permitted the preparation of several grams of the crystals. In this process, it was essential that oxygen be excluded. The oxygen uptake of the irradiated products was thought to be largely due to the oxidation of products other than the vitamin for much oxygen could be absorbed without a corresponding loss of potency. Provisionally, they gave the name *calciferol* to the crystals, recognizing the possibility that they might not be a single compound. This substance melted at 123-125°C. and had $[\alpha]^{5461}_{20°}=+260°$. The absorption spectrum showed a maximum at 2700A and an inflection at 2600A indicative of a second maximum. The elementary analysis and molecular weight determination indicated the substance to be an isomer (or a mixture of isomers) of ergosterol. Partially successful esterifications indicated the presence of an alcohol group. They were then uncertain as to whether the calciferol was a product of the original irradiation or one which had been altered by the heat employed in the subsequent distillation. The purity of these calciferol crystals was questioned by Bills, McDonald, Be Miller, Steel and Nussmeier.[112]

Meanwhile at Göttingen crystals were also obtained and called D_1.[113]

The irradiation products obtained under conditions of little or no over-irradiation, after being freed from unchanged ergosterol, were allowed to react with citraconic anhydide at room temperature. That portion which had reacted was removed after three days and the solvent evaporated from the remainder. The residue could be easily recrystallized, as long needles melting at 124-5°C. and subliming in high vacuum at 135°C. They had an absorption band with a maximum at 2650-2700A and were isomeric (composition and molecular weight) with ergosterol. The limiting antirachitic dose was 0.025γ. The crystals had a high positive rotation, in acetone or alcohol, $[\alpha]^{5461}_{20°}=+171°$ Samples made by the method of Reerink and van Wijk, however, showed a specific rotation of but +30°. D_1 seemed, furthermore, different from the crystals obtained in England since after ten recrystallizations, the German product had a rotation of +159° and the English of +260°. Windaus suggested that it might be that the only change involved was a steric one leading to an increase in the spatial size of the molecule. But it was suggested that during overirradiation, the double bonds which form a conjugated system may be moved to positions further apart.[114] The combination of the crystals with maleic anhydride indicated the presence of a conjugated double bond. At room temperature the new crystals absorbed no oxygen in twelve hours.

It was soon found, however, that neither calciferol nor D_1 represented the pure antirachitic photoisomer of ergosterol. The English workers announced that[115] by fractional crystallization of the 3,5-dinitrobenzoate, their product

[111] Angus, T. C., Askew, F. A., Bourdillon, R. B., Callow, R. K., Fischmann, C., Philpot, J., and Webster, T. A., *Ibid,* **108B,** 340 (1931).

[112] Bills, C. E., McDonald, F. G., Be Miller, L. N., and Nussmeier, M., *J. Biol. Chem.,* **93,** 775 (1931).

[113] Windaus, A., Lüttringhaus, A., and Deppe, M., *Annalen,* **489,** 252 (1931); Windaus, A., *Proc. Roy. Soc.,* **108B,** 568 (1931).

[114] For evidence for this from refractive indices, see Von Auwers, K., and Wolter, E., *Nachr. Ges. Wiss. Göttingen, Math. Physik. Kl.,* 101 (1931); *Chem. Abs.,* **26,** 5844 (1932).

[115] Askew, F. A., Bruce, H. M., Callow, R. K., Philpot, J. St. L., and Webster, T. A., *Nature,* **128,** 758 (1931).

had been separated into an inactive substance, pyrocalciferol, formed by the action of heat during the distillation, and the true antirachitic compound, for which they retained the name calciferol. Thus their original or "old calciferol" had been calciferol contaminated with pyrocalciferol, which is again an isomer.

Windaus and Linsert, in a brief note,[116] announced the isolation of another compound, D_2 melting at 115-116°C. and having $[\alpha]_D=+85°$ in acetone. This was obtained by the dinitrobenzoate method from D_1 which was found to consist of D_2 and an isomeric alcohol.[117] D_2 also shows definite absorption at 2650A. New calciferol and D_2 are identical, but the old calciferol and D_1 were not. The former had as the second material pyrocalciferol (and probably also the contaminant of D_1) and the latter had as the second component an isomeric alcohol formed from ergosterol by irradiation.[118] This has been called lumisterol, or a sterol formed by light. The lumisterol has its absorption maximum at about 2700A and is the substance which, on irradiation with short wave-lengths, is converted to the substance with strong absorption at 2800A. It was readily shown that lumisterol and calciferol (D_2) in equimolar proportions would have the absorption spectrum of D_1. The English workers suggested that the substance *L* of Reerink and van Wijk may have been a mixture of calciferol (D_2) and one or more inactive irradiation products. It was next shown by Windaus, Dithmar and Fernholz,[119] by titrations with perbenzoic acid, that lumisterol contains three double bonds. It has no antirachitic action and is not toxic. By irradiation in ether with the unfiltered light from a magnesium arc, in which the longer rays predominate, it is converted, in part at least, into D_2. Thus it must be a transitory intermediate product in the conversion of ergosterol into D_2. From the English observations, it would seem that, if in this process the lumisterol is irradiated by too short wave-lengths, the reaction follows a different course, producing the substance which absorbs maximally at 2800A. That the substance which disappears when this absorption at 2800A is produced is not the vitamin had been shown previously by Windaus and Auhagen.[120]

It was not yet apparent why it was so necessary to eliminate oxygen during the irradiation since none of the products thus far described is readily attacked by it. It was believed both by Windaus and by the English group that the irradiation product attacked by oxygen is not the antirachitic material. In further studies, Windaus, von Werder, and Lüttringhaus[121] isolated a substance from the treatment of the irradiation product with citraconic anhydride. Because of the rapidity with which it reacts with that reagent (much greater than D_2) it was called tachysterol. Since it reacts rapidly with oxygen also, it seems to be the product which makes the exclusion of oxygen essential. That this material must be preserved in order to secure high yields of D_2 during irradiation seems to imply that it lies in the direct line of conversion of ergosterol into D_2.[122] Tachysterol lacks antirachitic action and is not toxic.

[116] Windaus, A., and Linsert, O., *Annalen,* **489,** 269 (1931); see also *Z. physiol. Chem.,* **203,** 70 (1931).

[117] This work has been reviewed by Lüttringhaus, A., *Chem. Ztg.,* **55,** 956 (1931).

[118] Detailed accounts of the preparation of new calciferol are given in *Proc. Roy. Soc.,* **109B,** 488 (1932) and of D_2 by Windaus, A., Linsert, O., Lüttringhaus, A., and Weidlich, G., *Annalen,* **492,** 226 (1932). For criticism, see Bills, C. E., and McDonald, F. G., *J. Biol. Chem.,* **96,** 189 (1932). For another method of obtaining the crystals, see Sumi, M., *J. Agr. Chem. Soc. Japan,* **12,** 1211 (1936); *Bull. Inst. Phys. Chem. Research (Tokyo),* **15,** 635 (1936); *cf.* also Francesconi, L., and Opisso, F., *Ann. chim. appl.,* **25,** 124 (1935); *Brit. Chem. Abs.,* **A,** 857 (1935); *Chem. Abs.,* **29,** 6254 (1935).

[119] Windaus, A., Dithmar, K., and Fernholz, E., *Annalen,* **493,** 259 (1932).

[120] Windaus, A., and Auhagen, E., *Z. physiol. Chem.,* **196,** 108 (1931).

[121] Windaus, A., von Werder, F., and Lüttringhaus, A., *Annalen,* **499,** 188 (1932).

[122] Inhoffen, H. H., and Hauptmann, H., [*Z. physiol. Chem.,* **207,** 259 (1932)] believe that in the presence of tachysterol. D_2 becomes slightly sensitive to air.

It has a high absorption maximum at 2800 A and further bands at 2680 and 2940A and is changed, in part at least, into D_2 when irradiated by the magnesium spark. It thus appears to be the substance built up by short-wave irradiation of ergosterol or of lumisterol. That it does not appear during the long-wave irradiation is probably due to the fact that it is formed only in low concentrations and immediately converted into D_2. The use of short waves, owing to lack of absorption, could probably only very slowly convert it into D_2.

It thus became apparent that five isomers of ergosterol are produced by irradiation and it became possible to place them in the sequence in which the transformations occur.[123] Slight differences in the order were suggested in these papers, the following being the sequence of changes given in the most recent paper of Setz.

$$\text{Ergosterol} \rightarrow \text{Lumisterol} \rightarrow \text{Tachysterol} \rightarrow D_2 \begin{cases} \nearrow \text{Suprasterol I} \\ \rightarrow \text{Suprasterol II} \\ \searrow \text{Substance 248} \end{cases}$$

The substance 248 is so called because it has an absorption maximum at 2480A. It may be recalled that this substance was originally mistaken for the vitamin by Pohl. It is a product of overirradiation and is not antirachitic but is toxic and sometimes called toxisterol.[124] Setz states that irradiation of any substance in the list leads to the formation of a mixture of all substances following it, but that the sequence cannot be reversed. Light of the longest wave-length, 3100A, capable of altering ergosterol gives rise to lumisterol after which further change is but slow. With the use of somewhat shorter wave-lengths, 2800A, the lumisterol stage is passed over and tachysterol is immediately produced. It is very sensitive to longer wave-lengths and is converted into D_2. Between 3000 and 3600A, it absorbs more than ten times as strongly as does ergosterol. The existence of this sequence may explain why the mercury arc light, when freed by a xylene filter from rays shorter than 2800A, forms chiefly the vitamin and lumisterol in fairly constant proportions. The shorter rays are necessary to convert the lumisterol into tachysterol. The magnesium light, 2780 to 2800A, yields practically no lumisterol but chiefly tachysterol and D_2, suggesting that the tachysterol may be formed without passing through lumisterol as an intermediate stage. Against this possibly oversimplified scheme is also the fact that on short irradiations during which but 10 per cent of the ergosterol has been altered, D_2 predominates in the mixture, although it might be expected that the first product, lumisterol, would predominate. In a product of longer irradiation (method of Reerink and van Wijk) with 50 per cent ergosterol conversion, there were found to be present about 40-50 per cent of lumisterol, 30-40 per cent of D_2, 40-50 per cent of tachysterol, 5-10 per cent of suprasterol II and possibly also traces of suprasterol I.

By the use of a monochromator, Bowden and Snow[125] recently showed that calciferol in cyclohexane is rapidly decomposed by the wave-length 2650A, but is not changed by 3130A or longer wave-lengths. The decomposition is independent

[123] Windaus, A., Lüttringhaus, A., and Busse, P., *Nachr. Wiss. Göttingen, Math. Physik Kl.* 150 (1932); *Chem. Abs.*, **27**, 2180 (1933); Windaus A., von Werder, F., and Lüttringhaus, A., *Annalen*, **499**, 188 (1932); Setz, P., *Z. physiol. Chem.*, **215**, 183 (1933).

[124] Laquer, F., and Linsert, O., *Klin. Wochschr.*, **12**, 753 (1933). Spectroscopic evidence by Dimroth indicates that ergosterol cannot form tachysterol without passing through lumisterol, *Ber.*, **70B**, 1631 (1937). See also Windaus, A., *Sitzber, preuss. Akad. Wiss. Physik-math. Kl., No. 9-12*, 104 (1937).

[125] Bowden, F. P., and Snow, C. P., *Proc. Roy. Soc.*, **115B**, 261 (1934).

of the presence of air. Ergosterol in cyclohexane was not altered by the wave-length 3130A but was rapidly converted into calciferol by 2967A. With 2650A, the yield of calciferol was decreased. Thin crystals of ergosterol were scarcely affected by 3650, 3130 or 2537A, but were rapidly transformed by 2967A.

Jendrassik[126] has claimed that ergosterol can be rendered antirachitic by irradiation with sunlight, yielding a preparation 2 per cent as potent as that produced by artificial ultraviolet sources. It has been found possible to irradiate ergosterol by ultraviolet rays which have passed through the epidermis of a day-old rat.[127]

Chemical Changes Occurring During the Irradiation of Ergosterol

It has been pointed out in the preceding discussion that the various irradiation products in the sequence of changes undergone by ergosterol are all isomers. The elucidation of the constitution of each of these, established in all of the most important features, has been accomplished by the application of chemical and physical methods. Among the physical methods have been the comparison of the data on ultraviolet absorption, refractive indexes and x-ray crystal structures of these products with those of related compounds of known constitution. The chemical attack has involved the identification of oxidation products, the determination of the number of double bonds in the various products by catalytic microhydrogenation methods and by perbenzoic acid titrations, and the determination of their conjugation by the maleic anhydride reaction. The number of rings present was found by selenium dehydrogenations followed by the identification of the products. Finally, the thermal decomposition products have been studied. The details of the historical development lie beyond the scope of this discussion.[128]

It was first shown that the double bond (C_{22} to C_{23}) in the side-chain is unaltered during the transformations, since ergosterol, lumisterol, tachysterol, D_2 and suprasterol I can each yield methylisopropylacetaldehyde on suitable treatment.[129] The changes must then be stereochemical or associated with the positions and stability of the double bonds within ring B of ergosterol.

Three double bonds were found present in lumisterol,[130] and studies of the oxidation products indicated them to be in substantially the same positions as in ergosterol, a result supported also by dehydrogenation experiments by Dimroth. Only a stereoisomeric change remains as a possibility.[131] This was at first thought to consist in an epimerization of the hydroxyl group at position 3, but this has been shown unlikely by the observation that the unsaturated hydrocarbons produced by the dehydration of ergosterol and lumisterol by phosphoryl chloride are different.[132] Dimroth[133] has shown by a comparison of the absorption spectra

[126] Jendrassik, A., *Biochem. Z.*, **252**, 205 (1932).

[127] Lucas, N. S., *Biochem. J.*, **27**, 132 (1933).

[128] For detailed reviews, see Lettré, H., *Annalen*, **511**, 280 (1934); Callow, R. K., *Sci. J. Roy. Coll. Sci.*, **4**, 41 (1934); Rosenheim, O., and King, H., *Chem. & Ind.*, 196, (1934); 699 (1935); Nicola, O., *Rev. Med. Latin-Am.*, **220**, 358 (1934); **231**, 279; *Chem. Abs.*, **29**, 8075 (1935); Linsert, O., *Med. Chem. Forschungstatten I. G. Farbenind.*, **2**, 281 (1934); Rygh, O., *Tids. Kjemi Bergvesen*, **14**, 26 (1934); Windaus, A., *E. Merck's Jahresber.*, **50**, 3 (1936); Ruzicka, L., and Goldberg, M. W., *Helv. Chim. Acta*, **18**, 434 (1935); Schmidt, O., *Ber.*, **68B**, 1658 (1935); Heilbron, I. M., and Spring, F. S., *Chem. & Ind.*, 795 (1935); *Current Sci.*, **5**, 69 (1936); Fieser, L. F., "Chemistry of Natural Products Related to Phenanthrene," Reinhold, 2nd. ed., 177 (1937); Heilbron, I. M., *Chimie et industrie*, **39**, 19 (1938); Bills, C. E., *J. Am. Med. Assoc.*, **110**, 2150 (1938).

[129] Guiteras, A., *Annalen*, **494**, 116 (1932).

[130] Dimroth, K., and Möller, E. F., *Ber.*, **68B**, 539 (1935); Heilbron, I. M., Spring, F. S., and Stuart, P. A., *J. Chem. Soc.*, 1221 (1935); Haslewood, G., and Roe, E., *J., Chem. Soc.*, 465 (1935).

[131] More recent proof is due to Burawoy, A., *J. Chem. Soc.*, 409 (1937), and Heilbron, I. M., Moffet, G. L., and Spring, F. S., *J. Chem. Soc.*, 411 (1937).

[132] See, however, Callow, R. K., and Young, F. G., *Proc. Roy. Soc.*, **157A**, 194 (1936).

of dehydrolumisterol and dehydroergosterol, and by other chemical evidence, that the change in configuration occurs at the methyl group of C_{10}.[134] This persists in the succeeding products as well and Dimroth attributes the inability of the irradiation products to combine with digitonin to the spatial arrangement of the methyl group at C_{10} produced in the first transformation of the series.

A most significant observation by Lettré [135] showed tachysterol to contain the equivalent of four double bonds.[136] This could result only from the opening of a ring, reducing the number of rings in the system from four to three. For a time it was believed that in the conversion of tachysterol to D_2 a fourth ring is reformed. Unfortunately, it was not possible to obtain crystalline dehydrogenation products which might yield information as to the number of rings. However, it was established that D_2 also contains four double bonds by hydrogenation and by perbenzoic acid titrations.[137] Müller showed that it contained three of its double bonds in a conjugated system and differed only from tachysterol in the location of these bonds. Rosenheim and King [138] were of the opinion that the breaking of the ring in tachysterol formation took place between C(5) and C(10), resulting in the unusual formation of a ten-membered ring. This view was based upon x-ray evidence of Bernal,[139] which appeared to indicate an essential similarity of the unit cells of all of the irradiation products, the length of the molecule not being affected by the intramolecular changes. Proof that this is incorrect and that it is the bond between positions 9 and 10 which is broken was furnished by Lettré and by Heilbron and Spring [140] by the study of the products of the oxidation of D_2. In this work it was established that there must be a double bond in calciferol between positions 5 and 6. Furthermore, Windaus and Thiele by a study of certain degradation products and their maleic anhydride addition compounds located the remaining double bonds so that the structure of D_2 is that represented below.[141]

The thermal decomposition products of the D_2, pyrocalciferol and isopyrocalciferol are formed by a process involving a ring closure,[142] since the equivalent of a double bond disappears. The process occurs in such a manner as to re-form the original sterol ring system. There is evidence that a ring closure occurs also in the formation of suprasterol I by overirradiation but a different ring system, possibly containing a spirocyclopentane ring, is formed.[143]

Pyrocalciferol irradiated forty hours with magnesium light in peroxide-free ether yields photopyrocalciferol, and isopyrocalciferol similarly gives a photoisopyrocalciferol. Such changes are due to the conjugated system of two double bonds between C_5 and C_6 and between C_7 and C_8 in ring B, found also

[133] Dimroth, K., *Ber.*, **69**, 1123 (1936).

[134] Windaus, A., and Dimroth, K., *Ber.*, **70B**, 376 (1937).

[135] Lettré, H., *Annalen*, **511**, 280 (1934); *Angew. Chem.*, **47**, 736 (1934).

[136] See also Kuhn, R., and Möller, E. F., *Angew. Chem.*, **47**, 145 (1934).

[137] Müller, M., *Z. physiol. Chem.*, **233**, 223 (1935); Fernholz, E., *Annalen*, **499**, 198 (1932); Ahrens, G., Fernholz, E., and Stoll, W., *Ibid.*, **500**, 109 (1933); Heilbron, I. M., Samant, K. M., and Spring, F. S., *Nature*, **135**, 1072 (1935); Windaus, A., and Thiele, W., *Annalen*, **521**, 160 (1935).

[138] Rosenheim, O., and King, H., *Chem. & Ind.*, 699 (1935).

[139] Bernal, J. D., *Nature*, **129**, 277 (1932); Bernal, J. D., and Crowfoot, D., *Chem. & Ind.*, **54**, 701 (1935).

[140] Heilbron, I. M., and Spring, F. S., *Chem. & Ind.*, 795 (1935). The Windaus structures are corroborated by refractometric studies by von Auwers, K., [*Annalen*, **533**, 255 (1938)], as well as by other recent work of Heilbron, I. M., Kennedy, T., Spring, F. S., and Swain, G., [*J. Chem. Soc.*, 869 (1938)].

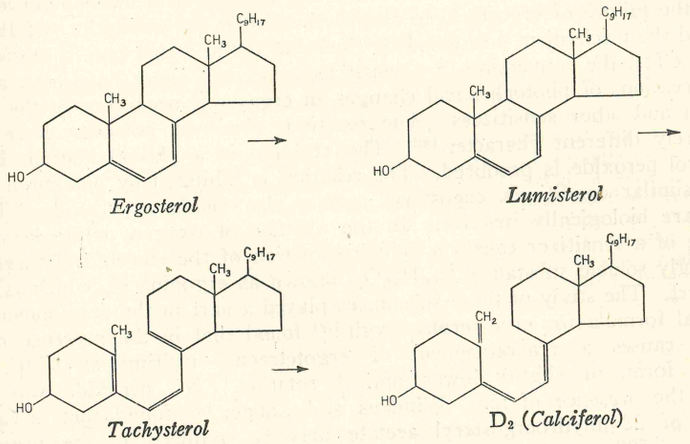
[141] See also Heilbron, I. M., Jones, R. N., Samant, K. M., and Spring, F. S., *J. Chem. Soc.*, 905 (1936); Windaus, A., and Grundmann, W., *Annalen*, **524**, 295 (1936); von Reichel, S., and Deppe, M., *Z. physiol. Chem.*, **239**, 143 (1936).

[142] Busse, P., *Z. physiol. Chem.*, **214**, 211 (1933); Müller, M., *Ibid.*, **233**, 223 (1935).

[143] Müller, M., *Z. physiol. Chem.*, **233**, 223 (1935).

in ergosterol, 22-dihydroergosterol, 7-dehydrocholesterol and 7-dehydrositosterol. Pyrocalciferol and isopyrocalciferol differ from ergosterol and lumisterol in having a different steric arrangement at C_9. The irradiation of the pyro- compounds converts the conjugated system into a system of isolated double bonds, which may again be converted by heat into the original conjugated system. No steric rearrangement occurs at C_{10}. Instead, a double linkage is shifted from ring B to ring A.

Fuchs and van Niekerk [144] observed that crystalline D_2 kept in air in darkness undergoes some changes involving the development of a yellow color and the loss of ultraviolet absorption. Little is yet known regarding the structure of suprasterol II or of the substance 248 (toxisterol). The structures of the various irradiation products are summarized by the following formulas:



The positions of the double bonds in tachysterol are perhaps still uncertain. If the conversion of this to vitamin D_2 is as indicated, it is conceivable that the absorption of light by tachysterol involves the liberation of atomic hydrogen which later adds on again at position 9. It would be interesting to learn whether its presence could be detected during the photochemical process by the aid of the para hydrogen conversion. Grundmann gives evidence for proposing that the double bonds in tachysterol should be placed as shown rather than in the positions 1,10; 5,6 and 7,8.[145]

Recently, attention has been paid to the effects of irradiation on the surface pressures and surface potentials of unimolecular films of ergosterol.[146] The evidence indicates a change in the shape of the molecules as the irradiation proceeds. The results were attained before the structures indicated above had been determined and they have not been correlated with them as yet.

There has not as yet been achieved a direct synthesis of D_2. Natelson and Gottfried, however,[147] have synthesized 4-β-phenylethylindane, the structure proposed for the calciferol nucleus.

[144] Fuchs, L., and van Niekerk, J., *Biochem. Z.*, **277**, 32 (1935).

[145] Grundmann, W., *Z. physiol. Chem.*, **252**, 151 (1938).

[146] Fosbinder, R. J., *Proc. Roy. Soc.* **139A**, 93 (1933); Danelli, J. F., and Adam, N. K., *Biochem. J.*, **28**, 1583 (1934).

[147] Natelson, S., and Gottfried, S. P., *J. Am. Chem. Soc.*, **58**, 1432 (1936).

The activation energy of the conversion of ergosterol into D_2 has recently been calculated from quantum mechanical considerations.[148]

The activation energy sets the long wave-length limit for the conversion. If there is merely the breaking of a C—H linkage on C_{18} followed by a migration of the hydrogen atom to the carbon in position 9, the activation energy is 92.3 kcal. which agrees well with the usually accepted long wave-length limit of about 3100A. The authors considered many other mechanisms and found the one involving the least energy of activation to require 72 kcal. which would place the long wave-length threshold at about 3950A. The suggested mechanism does not take into account the stereochemical change involved in the formation of lumisterol. It may be that this requires a somewhat greater energy of activation and sets the observed wave-length limit.

That a longer threshold than 3100A has not been experimentally observed may be due to the failure of ergosterol to absorb the longer wave-lengths. If this is the case and the mechanism postulated by Sherman is the actual one, it might be possible to effect the conversion in a sensitized process. There have been a number of observations of photochemical changes in ergosterol occurring in the presence of eosin and other sensitizers. The reactions observed, however, have been of an entirely different character.[149] The reaction is a photoöxidation, in which ergosterol peroxide is produced. The reaction is inhibited by potassium cyanide. Under similar conditions, ergosteryl acetate also yields a peroxide. The peroxides are biologically inactive. In the absence of oxygen, white light in the presence of a sensitizer causes a dehydrogenation of the sterol, and there results a sparingly soluble substance, $C_{56}H_{86}O_2$, known as ergopinacol, which is biologically inert. The study of these substances played a part in the development of the structural formula for ergosterol. Rygh[150] found that in the presence of eosin, sunlight causes a rearrangement of ergotetraene, melting at 97°C. to an isomeric form, of slighty lower optical rotation. No peroxide was formed even in the presence of air. Windaus and Langer[151] found that an alcoholic solution of 22-dihydroergosteryl acetate may be oxidized in the presence of eosin by a 500-watt lamp to a peroxide. The free 22-dihydroergosterol itself behaves similarly. Dimroth[152] also has shown that, in alcohol, dehydrolumisterol acetate reacts with eosin in sunlight to give a so-called pinacol, but that lumisterol and pyrocalciferol do not behave in this way. Dehydroergosterol acetate and isopyrocalciferol yield the same pinacol when treated in this manner. It differs from that[153] obtained from dehydrolumisterol.

According to Montignie[154] sunlight does not influence the reactions of cholesterol with uranyl nitrate, silver nitrate, mercury oxide, iodoform or mercuric iodide.

Other Antirachitic Compounds

Windaus and Langer[155] made the important observation that ergosterol in which the double bond in the side chain has been saturated, *i.e.*, 22-dihydroergosterol, can also function as a provitamin, although the antirachitic activity of the irradiation product is but one-thirtieth that of D_2. This means that the double bond in the side chain does not play a part in the sequence of irradiation changes in the case of ergosterol. This observation was made before the evidence presented in the preceding discussion of the mechanism of the formation of D_2.[156] It led to the suggestion that it might be possible to prepare an antirachitic substance from cholesterol could there first be introduced into the molecule a double bond in position 7, 8, thus rendering the molecule analogous to that of ergosterol in the features essential to the conversion. This was accomplished by Windaus, Lettré and Schenck,[157] who succeeded in preparing the benzoate of 7-dehydrocholesterol. The product of its irradiation even in a crude form had a high antirachitic potency, approximately half that of the product from ergosterol. This work provided a justification of the objections that had been raised by a relatively few earlier workers to the almost universally accepted view that ergosterol was the precursor of the vitamin D.

Jendrassik and Kemenyffi[158] had been of the opinion that a removal of the provitamin from a cholesterol preparation destroys an equilibrium between cholesterol and a provitamin leading to the conversion of more cholesterol into provitamin. They had no conception of the nature of the provitamin but suggested that it might be ergosterol. Bills, Honeywell and MacNair[159] maintained that samples of cholesterol contained traces of an activatable substance other than ergosterol, a view not shared by Kon, Daniels and Steenbock.[160] Koch, Koch and Ragins[161] asserted that even purified cholesterol could to a slight extent be activated and that it might be made more activatable by heating it slightly above the melting point. Koch, Koch and Lemon[162] concluded from spectrographic studies that ordinary cholesterol contains only about one-thousandth part of ergosterol[162a] but was more capable of activation than could be accounted for by this ergosterol, so that some other activatable substance must be present. At the time, these views attracted relatively little attention. Yoder[163] has recently called attention to a chemical method of obtaining antirachitic material from cholesterol by means of sulfur trioxide and acetic anhydride. DeCaro[164] claimed the non-saponifiable fraction of lanolin acquires antirachitic properties on irradiation. Gustavson[165] found that the extraction of irradiated cholesterol with liquid ammonia gave a yellow resinous material a quarter of a milligram of which gave complete protection against rickets when incorporated in the McCollum rachitic diet.

The brilliant results of the ergosterol investigations diverted attention from cholesterol and it came to be rather generally believed that D_2 was identical with the vitamin from natural sources. This view was maintained until an interesting difference in the response of rachitic animals of different species to the action of the antirachitic vitamin from various sources showed the non-identity of D_2 with the natural vitamin of cod-liver oil.[166] Hess and Supplee[167] observed that chickens are regularly protected against leg weakness by the addition of

[148] Owen, J. R., and Sherman, A., *J. Am. Chem. Soc.*, **59**, 763 (1937).

[149] Windaus, A., Borgeaud, P., and Brunken, J., *Nachr. Ges. Wiss. Göttingen, Math. Physik Kl.*, 313 (1927); Windaus, A., and Brunken, J., *Annalen*, **460**, 225 (1928); Windaus, A., and Borgeaud, P., *Annalen*, **460**, 235 (1928); compare Meyer, K., *J. Biol. Chem.*, **103**, 607 (1933).

[150] Rygh, O., *Z. physiol. Chem.*, **185**, 99 (1929).

[151] Windaus, A., and Langer, R., *Annalen*, **508**, 105 (1933).

[152] Dimroth, K., *Ber.*, **69B**, 1123, 1631 (1936).

[153] Windaus, A., and Dimroth, K., *Ber.*, **70B**, 376 (1937).

[154] Montignie, E., *Bull. Soc. Chim.*, **1**, 290 (1934); *Chem. Abs.*, **28**, 5466 (1934).

[155] Windaus, A., and Langer, R., *Annalen*, **508**, 105 (1933).

[156] The product has recently been isolated through the nitrobenzoate as crystalline D_4., Windaus, A., and Trautmann, G., *Z. physiol. Chem.*, **247**, 185 (1937).

[157] Windaus, A., Lettré, H., and Schenck, F., *Annalen*, **520**, 98 (1935).

[158] Jendrassik, A., and Kemenyffi, A. G., *Biochem. Z.*, **189**, 180 (1927); **201**, 269 (1928).

[159] Bills, C. E., Honeywell, E. M., and MacNair, W. A., *J. Biol. Chem.*, **76**, 251 (1928).

[160] Kon, S. K., Daniels, F., and Steenbock, H., *J. Am. Chem. Soc.*, **50**, 2573 (1928).

[161] Koch, F. C., Koch, E. M., and Ragins, I. K., *J. Biol. Chem.*, **85**, 141 (1929).

[162] Koch, F. C., Koch, E. M., and Lemon, H. B., *J. Biol. Chem.*, **85**, 159 (1929).

[162a] Actually 7-dehydrocholesterol has a similar absorption spectrum.

[163] Yoder, L., *J. Biol. Chem.*, **116**, 71 (1936); Eck, J. C., Thomas, B. H., and Yoder, L., *Ibid.*, **117**, 655 (1937); Eck, J. C., and Thomas, B. H., *Ibid.*, **119**, 621 (1937).

[164] De Caro, M., *Boll. soc. ital. biol. sper.*, **7**, 1097 (1932); *Chem. Abs.*, **27**, 1035 (1933).

[165] Gustavson, R. G., *J. Colorado-Wyoming Acad. Sci.*, **1**, 23 (1929); *Chem. Abs.*, **26**, 3547 (1932).

[166] This work was reviewed by Holmes, A. D., *New England J. Med.*, **204**, 211 (1931); *Chem. Abs.*, **26**, 179 (1932).

[167] Hess, A. F., and Supplee, G. C., *Proc. Soc. Exptl. Biol. Med.*, **27**, 609 (1930).

1 per cent of cod-liver oil to their rations. A supplement of irradiated ergosterol equivalent in rat experiments to many times this amount of vitamin D failed, however, to afford protection. In experiments on White Leghorns, Massengale and Nussmeier[168] found it necessary to administer a quantity of irradiated ergosterol equivalent by rat assay to 200 per cent of cod-liver oil in order to produce the effects which could be produced by a 2-per cent (by rat assay) addition of cod-liver oil. Similar results were reported by Mussehl and Ackerson.[169] In the many subsequent confirmatory observations, which need not be discussed in detail, it was suggested by some that the presence of vitamin A in the cod-liver oil might by a synergistic action account for the greater effectiveness of the natural over the artificial vitamin.[170] This, however, was shown not to be the case by Russell and Klein,[171] and the opinion that the vitamin of cod-liver oil is different from the artificial vitamin was shared by Bills.[172] Thus there appeared to be two forms of the vitamin (but this number has since been increased). Amounts of the two that were equally effective for the rat were not equally effective for the chicken, far less of the natural than of the artificial vitamin being required for that species.[173]

The human seems intermediate between the chick and the rat in its response. Hess, Lewis and Rivkin[174] found that about three rat units of an ergosterol preparation are clinically equivalent to one rat unit of cod-liver oil.[175] Drake,[175a] however, has found no essential difference in their effects on infants.

Products Related to Cholesterol as Precursors of the Natural D.

Waddell[176] as a result of extensive studies directed toward an explanation of the great effectiveness of direct irradiation of the chick in comparison with the effectiveness of irradiated ergosterol, suggested either that the course of the irradiation changes of ergosterol within the skin is different from that *in vitro* or that the precursor in the skin is not ergosterol. To decide this question, he irradiated crude cholesterol in order to study any products which might be formed in the skin by natural contaminants of cholesterol. It was found that the irradiated crude cholesterol gave better protection against leg weakness in chicks than did irradiated ergosterol, rat unit for rat unit. The idea that this might be ascribed to an improved absorption of ergosterol in the presence of

[168] Massengale, O. N., and Nussmeier, M., *J. Biol. Chem.*, **87**, 423 (1930).

[169] Mussehl, F. E., and Ackerson, C. W., *Poultry Sci.*, **9**, 334 (1930); *Chem. Abs.*, **26**, 2221 (1932).

[170] See, for example, Dalmer, O., von Werder, F., and Moll, T., *Z. physiol. Chem.*, **224**, 86 (1934).

[171] Russell, W. C., and Klein, D., *Poultry Sci.*, **10**, 269 (1930); *Chem. Abs.*, **26**, 2222 (1932).

[172] Bills, C. E., *Physiol. Rev.*, **15**, 1 (1935). The vitamin from irradiated cholesterol seems as effective as that from cod-liver oil for laying birds. Bethke, R. M., Record, P. R., Wilder, O. H. M., and Kennard, D. C., *Poultry Sci.*, **16**, 438 (1937); *Chem. Abs.*, **32**, 980 (1938).

[173] Other papers relating to these species differences: Russell, W. C., Taylor, M. W., and Wilcox, D. E., *J. Biol. Chem.*, **107**, 736 (1934); Dols, M., *IV Congr. intern. tech. chim. ind. agr. Bruxelles*, **1**, IC (1935); *Chem. Abs.*, **30**, 5267 (1936); Supplee, G. C., Flanigan, G. E., Kahlenberg, O. J., and Hess, A. F., *J. Biol. Chem.*, **91**, 773 (1931); Steenbock, H., Kletzien, S., and Halpin, J. G., *Ibid.*, **97**, 249 (1932); Tully, W. C., Hauge, S. M., Carrick, C. W., and Roberts, R. E., *Poultry Sci.*, **10**, 310 (1931); Hunter, J. E., Dutcher, R. A., and Knandel, H. C., *Ibid.*, **11**, 239 (1932); Branion, H. D., and Smith, J. B., *Ibid.*, **11**, 261 (1932); *Chem. Abs.*, **27**, 1032 (1933); King, E. J., Hull, H., and Hall, G. E., *Poultry Sci.*, **12**, 129 (1933); *Chem. Abs.*, **27**, 3504 (1933); DeVaney, G. M., Munsell, H., and Titus, H. W., *Poultry Sci.*, **12**, 215 (1933); *Chem. Abs.*, **27**, 5380 (1933); Halvorson, H. A., and Lachat, L. L., *J. Assoc. Official Agr. Chem.*, **19**, 598, 628, 637, 647 (1936).

[174] Hess, A. F., Lewis, J. M., and Rivkin, H., *J. Am. Med. Assoc.*, **94**, 1885 (1930); Hess, A. F., and Lewis, J. M., *Ibid.*, **99**, 647 (1932); **101**, 181 (1933). *Contra*, Bacharach, A. L., *Food*, **6**, 180 (1937); *Chem. Abs.*, **31**, 5415 (1937).

[175] See also Barnes, D. J., Brady, M. J., and James, E. M., *Am. J. Diseases of Children*, **39**, 45 (1930); Prather, E. O., Nelson, M., and Bliss, A. R., Jr., *Ibid.*, **42**, 52 (1931).

[175a] Drake, T. G. H., *Am. J. Diseases of Children*, **53**, 754 (1937).

[176] Waddell, J., *J. Biol. Chem.*, **105**, 711 (1934).

large amounts of cholesterol was excluded by subsequent experiments. When the cholesterol had been purified by refluxing half an hour with hot ethanol containing potassium hydroxide followed by treatment with charcoal, similar good results were obtained. Repeated irradiations of cholesterol with removal of the activated product gradually exhausted the activatability of the cholesterol, indicating that it was not the cholesterol itself which was the provitamin. When ergosterol was irradiated in the presence of purified cholesterol the vitamin produced was no more effective than that resulting from the irradiation of the ergosterol alone. These experiments were important in indicating that there is in crude cholesterol a provitamin other than ergosterol which is capable of yielding a vitamin more potent to chicks than that obtainable from ergosterol.

In crude ergosterol no provitamin other than ergosterol itself could be detected by Bills, Massengale, McDonald and Wirick,[177] in analogous experiments.

Further evidence, now known to have been erroneous, also stimulated the investigation of the non-identity of the vitamin in cod liver oil with that of irradiated ergosterol. Rygh[178] concentrated the vitamin from cod liver oil about 20,000 times and concluded the active product to show no absorption maximum between 2600 and 2700A. Various other properties also differed from those of D_2, which led him to conclude them to be different substances. Ender[179] reached similar conclusions from ultraviolet absorption studies of a concentrate from tuna fish liver oil.

The provitamin of crude cholesterol is destroyed during a purification through the dibromide. The provitamin content of the purified material may then be increased by heat treatment, according to Hathaway and Lobb.[180] This confirmed an earlier observation of Hathaway and Koch[181] who used a temperature of 200°C. At 300°C., however, the provitamin is materially destroyed within four hours. The provitamin was formed in the cholesterol fractions which were the most difficultly soluble in alcohol. There was no evidence of the formation of any ergosterol during the heat treatment and the vitamin produced on irradiation was in its effects on the chick more similar to the natural liver oil vitamin than that obtained by the irradiation of ergosterol. Absorption bands in the heated purified cholesterol were observed by Haman and Steenbock,[182] who also showed that the provitamin is one which yield a vitamin similar to that of the fish oils. They also observed that irradiated plant oils were less effective for chicks than irradiated animal fats, thus aiding in focusing attention upon a derivative of cholesterol as the natural provitamin.

By use of adsorption methods applied to a sample of cholesterol as acetate which contained 4.5 per cent of the new provitamin, Boer, Reerink, Van Wijk and van Niekerk[183] succeeded in isolating the provitamin, first as acetate and after saponification, as the free sterol. It was possible to show its identity with 7-dehydrocholesterol, both by a comparison of the properties of the samples, and by their biological activity after irradiation. By the use of similar chromato-

[177] Bills, C. E., Massengale, O. N., and Wirick, A. M., *J. Biol. Chem.*, **108**, 323 (1935).

[178] Rygh, O., *Nature*, **136**, 396 (1935).

[179] Ender, F., *Z. Vitaminforschung*, **2**, 241 (1933); **3**, 161 (1934); *Chem. Abs.*, **28**, 4103, 7422 (1934).

[180] Hathaway, M. L., and Lobb, D. E., *J. Biol. Chem.*, **113**, 105 (1936).

[181] Hathaway, M. L., and Koch, F. C., *J. Biol. Chem.*, **108**, 773 (1935).

[182] Haman, R. W., and Steenbock, H., *J. Biol. Chem.*, **114**, 505 (1936); see also Roffo, A. H., Calgano, O., and Roffo, A. E., Jr., *Bull. Soc. Chim. Biol.*, **17**, 203 (1935).

[183] Boer, A. G., Reerink, E. H., van Wijk, A., and van Niekerk, J., *Proc. Acad. Sci. Amsterdam*, **39**, 622 (1936); *Chem. Abs.*, **30**, 5635 (1936).

graphic methods, Brockmann[184] isolated the natural vitamin from tuna fish liver oils and from halibut liver oil.[185]

Windaus, Schenck and van Werder[186] showed that irradiation of 7-dehydrocholesterol in benzene with a magnesium spark gave a product of high antirachitic activity. Tachysterol-3 is first formed. The crude irradiation product was purified through the crystalline dinitrobenzoate and allophanate. These derivatives on saponification yielded the vitamin in the form of a non-crystallizing oil with an absorption maximum at 2650A, similar to that of D_2. The new material was called D_3. It was subsequently obtained in crystalline form by Schenck.[187] It melts at 82-4°C. and has $[\alpha]_D^{20} = +83.3°$. It will be noted that 7-dehydrocholesterol has the same disposition of double bonds in the ring B as has ergosterol and the vitamin produced by irradiation differs from D_2 only in the side-chain, the double bond at positions 22 to 23 and the methyl group at carbon 24 of D_2 being lacking in D_3. As first prepared, the rat potency of D_3 appeared somewhat lower than that of D_2, 30×10^6 I.U. per gram as compared with 40×10^6.[188] Subsequently, however, Brockmann and Busse[189] found D_3 crystals from tuna fish liver to have 40,000 I.U. per mg.

Irradiation of 7-dehydrocholesterol with wave-lengths longer than 2800A gives lumisterol-3 which probably differs from lumisterol only in the steric arrangement of groups at carbon atom 10.

The contaminant of cholesterol obtained from spinal cords was found to be 7-dehydrocholesterol or some similar derivative with two double bonds in ring B by Koch and Koch.[190] They believed, however, that the provitamin in heated cholesterol is some quite different material which does not have these double bonds. This material might be present in crude cholesterol, since it was possible to eliminate the impurity with the characteristic absorption spectrum from spinal cord cholesterol and still have a product so potent that, after irradiation, 0.1 to 3.0 mg. equals one rat unit. It was pointed out that the antirachitic potency which can be attained by a provitamin is conditioned not only by the two double bonds in ring B but also by the nature of the side-chain.

The provitamin of pig skin is 7-dehydrocholesterol according to Windaus and Bock,[191] who isolated it as dinitrobenzoate. That of egg yolk sterols is ergosterol.[192] It is possible that there is no ergosterol in skin, since its past identification had been based solely upon the absorption spectrum, which is similar to that of 7-dehydrocholesterol.

An analogous compound, 7-dehydrositosterol, prepared by Wunderlich,[193] was found capable of yielding an antirachitic substance on irradiation, but its potency was forty times less than that of D_2. The dehydrositosterol also undergoes the photosensitized conversion to a pinacol type of bimolecular compound.

[184] Brockmann, H., *Z. physiol. Chem.*, **241**, 104 (1936).

[185] Brockmann, H., *Z. physiol. Chem.*, **245**, 96 (1937). See also Haslewood, G., and Drummond, J. C., *Chemistry and Industry*, 598 (1936); Simonds, E., and Zucker, T., *J. Am. Chem. Soc.*, **58**, 2655 (1936); Neracher, O., and Reichstein, T., *Helv. Chim. Acta*, **19**, 1382 (1936). Two or more forms of vitamin may exist in fish oils, according to Bills, C. E., Massengale, O. N., Imboden, M., and Hall, H., *J. Nutrition*, **13**, 435 (1937); Hickman, K. C. D., and Gray, E. LeB., *Ind. Eng. Chem.*, **30**, 796 (1938).

[186] Windaus, A., Schenck, F., and von Werder, F., *Z. physiol. Chem.*, **241**, 100 (1936); Windaus, A., Deppe, M., and Wunderlich, W., *Annalen*, **533**, 118 (1937).

[187] Schenck, F., *Naturwiss.*, **25**, 159 (1937). D_3 is said to be twice as active as D_2 on infants by Brockmann, H., *Klin. Wochschr.*, **16**, 1383 (1937).

[188] Zucker, T. F., Simona, E. J., Colman, H. C., and Demarest, B., *Naturwiss.*, **26**, 11 (1938).

[189] Brockmann, H., and Busse, A., *Naturwiss.*, **26**, 122 (1938). See also Ramp, D. G., and Marshall, I. H., *J. Nutrition*, **15**, 525 (1938).

[190] Koch, E. M., and Koch, F. C., *J. Biol. Chem.*, **116**, 757 (1936).

[191] Windaus, A., and Bock, F., *Z. physiol. Chem.*, **245**, 168 (1936).

[192] Windaus, A., and Stange, O., *Z. physiol. Chem.*, **244**, 218 (1936).

[193] Wunderlich, W., *Z. physiol. Chem.*, **241**, 116 (1936).

Urushibara and Ando[194] described the photochemical dehydrogenation of an alcoholic solution of 7-dehydrocholesterol by sunlight in the presence of eosin. After a week there were obtained flocculent needles considered to be, in analogy with the behavior of ergosterol, 7-dehydrocholestenopinacone.

A search has been made for other provitamins. Weinhouse and Kharash[195] irradiated a series of tertiary alcohols or their dehydration products obtained by the action of various Grignard reagents on 7-ketocholesteryl acetate. The only one which showed slight antirachitic activity when irradiated was 7-isobutylidenecholesterol. Uraki[196] observed that irradiation of α-cholatrienic acid in chloroform for nine hours changed the specific rotation from −22.63° to +2.4°. The product was a non-crystallizing resin which could be hydrogenated to cholanic acid. The β-choladienic acid from desoxycholic acid was not altered by ultraviolet rays. It appeared that the point of attack in cholatrienic acid was the B ring, a shifting of the double bond occurring. Kikuzawa[197] reported the irradiated methyl α-cholate to have a slight antirachitic action. The β- derivative had less.

Rygh[198] recently found evidence for the occurrence in butter and ether extracts of hay and beef liver of an antirachitic substance which differed from other antitrachitic vitamins in occurring to a larger extent in the saponifiable than in the unsaponifiable fraction. Kon and Booth[199] observed that the saponification of butter caused a loss of 80 per cent of its antirachitic potency.

The sterols from cacao-bean butter (theosterols) can be made antirachitic by irradiation.[200]

A recent review of the relative potencies for the rat and the chick of the antirachitic substances produced, chemically, by irradiation, or occuring in natural sources (particularly the fish liver oils of different species), has been given by Bills.[201] Grab[202] concluded the crystalline product from irradiated 7-dehydrocholesterol to be equivalent in its effects on the rat and the chick to a crystalline product isolated from tuna-liver oil. This material he called D_3. The difference of a methyl group between irradiated 7-dehydrocholesterol and irradiated 22-dihydroergosterol resulted in but little difference in physiological activity. Sterols with 29 carbon atoms are scarcely to be considered natural provitamins since the activities of 7-dehydrositosterol and 7-dehydrostigmasterol were very low. D_2 is somewhat less potent on the rat and considerably less potent on the chick than D_3.

Colorimetric methods are of limited use for the assay of vitamin D_2. These are based upon the spectrophotometric measurement of the intensity of an absorption band at 5000A produced by the addition of antimony trichloride or of one produced by aluminum chloride.[203] A color test with sodium selenite is given

[194] Urushibara, Y., and Ando, T., *Bull. Chem. Soc. Japan*, **11**, 802 (1936); **12**, 495 (1937); *Chem. Abs.*, **31**, 2100 (1937). For similar work on 2,4-cholestadiene, see Skau, E. L., and Bergmann, W., *J. Am. Chem. Soc.*, **60**, 986 (1938); Butenandt, A., and Kudssus, H., *Z. physiol. Chem.*, **253**, 1, 224 (1938).

[195] Weinhouse, S., and Kharash, M. S., *J. Org. Chem.*, **1**, 490 (1936).

[196] Uraki, J., *Z. physiol. Chem.*, **221**, 40 (1933); *Chem. Abs.*, **28**, 168 (1934).

[197] Kikuzawa, T., *Z. physiol. Chem.*, **220**, 54 (1933); see also Okii, I., *J. Biochem. Japan*, **18**, 45 (1933); *Chem. Abs.*, **27**, 5425 (1933).

[198] Rygh, O., *Nature*, **133**, 533 (1934); *Z. Vitaminforschung*, **3**, 164 (1934); *Chem. Abs.*, **28**, 7315 (1934).

[199] Kon, S. K., and Booth, R. G., *Biochem. J.*, **27**, 1302 (1933); **28**, 111 (1934).

[200] Labbe, H., de Balsac, F., and Lerat, R., *Bull. soc. therap.*, **35**, 71 (1930); *Chem. Abs.*, **24**, 982 (1930); **25**, 729 (1931); Knapp, A. W., and Coward, K. H., *Biochem. J.*, **29**, 2728, (1935).

[201] Bills, C. E., *Cold Spring Harbor Symposia Quant. Biol.*, **3**, 328 (1935); *J. Am. Med. Assoc.*, **108**, 13 (1937). *Cf.* also Hume, E. M., *Nutrition Abstracts and Reviews*, **6**, 891 (1937); von Wendt, G., *Voprosy Pitaniya*, **5**, No. 4, 31 (1936); *Chem. Abs.*, **31**, 2659 (1937).

[202] Grab, W., *Z. physiol. Chem.*, **243**, 63 (1936).

[203] Brockmann, H., and Chen, Y. H., *Z. physiol. Chem.*, **241**, 129 (1936); Emmerie, A., and van Eekelen, M., *Acta Brevia, Neerland. Physiol., Pharmakol. Microbiol.*, **6**, No. 9-10, 133 (1936); *Chem. Abs.*, **31**, 1448 (1937); Halden, W., and Tzoni, H., *Nature*, **137**, 909 (1936); *Naturwiss.*, **24**, 296 (1936); Tzoni, H., *Biochem. Z.*, **287**, 18 (1936); Brückner, J., *Biochem. Z.*, **270**, 346 (1934); Wait, R., *Pharm. Zentralhalle*, **78**, 237 (1937).

by D_2 but not by cholesterol before or after irradiation.[204] Biological assay methods, however, have been employed most frequently in the development of our knowledge of these substances. Their discussion, as well as that of the effects of the sterol irradiation products on the mineral metabolism, lies beyond the scope of this work.

Physiological Effects. In general, the administration of pure irradiation products leads to the effects on blood calcium and phosphorus and on bone calcification that result on general irradiation of the experimental animal. It would add but little to recount the many earlier experiments in which indefinite irradiation products, frequently contaminated with either inert or with predominantly toxic products, had been used.[205]

Robinson and Rosenheim[206] found vitamin D to exert no demonstrable action on the calcification or decalcification of bone slices *in vitro*, but Venar and Todd[207] report that the extent and density of mineralization of bone fragments from rachitic mice may be increased by the addition of small amounts of an aqueous emulsion of irradiated ergosterol to the calcifying medium in which the bones are immersed. Similar effects may be attained by the use of cod-liver oil or by irradiating the cultures by a sunlamp.[208]

Harris[209] believes the vitamin to function by increasing the net absorption of calcium and phosphates from the intestine, thus tending to raise the level of the blood calcium or phosphate. The latter rise automatically brings about increased calcification in sites provided with the bone-calcifying enzyme, phosphatase. Hottinger[210] suggested that it renders innocuous some inhibitor of calcium assimilation, possibly an enzyme capable of decomposing glycerophosphates or hexosephosphates. Taylor and Weld[211] were of the opinion that, at least in young dogs, there is no evidence that irradiated ergosterol increases calcium absorption; indeed they state that even small doses increase the excretion of calcium.

One speculation as to the mechanism by which the vitamin functions regards it as liberating inorganic phosphorus from the lipins of the body, a deficiency of inorganic phosphate being regarded as the essential cause of rickets.[212] Nicolaysen[213] finds that in rachitic rats, inorganic phosphorus is reduced in the muscles, liver and kidneys. Massive doses of the vitamin increased it to normal, but therapeutic doses caused only a slight increase of the inorganic phosphorus of the kidney.[214] In D deficient rats, the percentage of inorganic phosphorus in the red blood cells is reduced, but that of easily hydrolyzable phosphoric esters is increased.[215] Warkany[216] observed that rabbits which usually excrete no phosphates, eliminate large quantities in the urine within 48 hours after the administration of 30 to 100 mg. of irradiated ergosterol in their food.

In artificial cultures of the skeletal tissues of the embryo chick, phosphatase

[204] Levine, V. E., and McKay, F. M., *Proc. Soc. Exp. Biol. Med.*, **33**, 546 (1936).

[205] See Laurens, H., "The Physiological Effects of Radiations." New York, The Chemical Catalog Co., Inc., (Reinhold Publishing Corp.) 1933. For more recent studies, Crimm, P. D., Strayer, J. W., Watson, H. L., and Heimann, G., *Am. Rev. Tuberc.*, **28**, 202 (1933); *Chem. Abs.*, **28**, 806 (1934); Morgan, A. F., Garrison, E. A., Householder, H., Hansen, A. M., Seberger, M. V., Watenpaugh, J. T., Felsher, A., and Long, N. L., *Univ. California Pub. Physiol.*, **8**, 61 (1934); *Chem. Abs.*, **28**, 7315 (1934); Freeman, S., *Am. J. Physiol.*, **115**, 701 (1936); Johnson, R. M., *J. Clin. Investigation*, **16**, 223 (1937).

[206] Robison, R., and Rosenheim, A. H., *Biochem. J.*, **28**, 684 (1934).

[207] Venar, Y., and Todd, T. W., *J. Lab. Clin. Med.*, **22**, 221 (1936); see also Dejust, L. H., *Rev. actinologie physiotherap.*, **6**, 1 (1931); *Chem. Abs.*, **26**, 2792 (1932).

[208] Yoshitomi, M., *J. Biochem. Japan*, **21**, 37 (1935); *Chem. Abs.*, **29**, 2590 (1935).

[209] Harris, L., *Lancet*, **I**, 1031 (1932); *Chem. Abs.*, **27**, 2187 (1933).

[210] Hottinger, A., *Naturwiss.*, **16**, 484 (1928).

[211] Taylor, N. B., and Weld, C. B., *Trans. Roy. Soc. Canada*, **26**, 9 (1932); *Chem. Abs.*, **27**, 1922 (1933).

[212] McGowan, J. P., Cunningham, I. J., and Auchinachie, D. W., *Biochem. J.*, **25**, 1295 (1931); McGowan, J. P., *Ibid.*, **27**, 943 (1933).

[213] Nicolaysen, R., *Biochem. J.*, **30**, 1329 (1936); *see also Biochem. J.*, **31**, 101, 105, 107, 122, 328 (1937).

[214] See also Jones, J. H., and Cohn, B. N. E., *J. Nutrition*, **11**, 293 (1936); Duffau, R., [*Compt. rend. soc. biol.*, **124**, 1194 (1937)] finds an increase of about 10% in the orthophosphates of muscles in rickets.

[215] Von Euler, H., and Brandt, K., *Z. physiol. Chem.*, **240**, 215 (1936).

[216] Warkany, J., *Klin. Wochschr.*, **9**, 2152 (1930); *Chem. Abs.*, **25**, 1877 (1931).

appears early.[217] Heymann[218] found that under the influence of irradiated ergosterol, phosphatase activity *in vitro* is unchanged, but ultraviolet irradiation caused inhibition of the enzyme in about 40 per cent of the tests. The enzyme is greatly increased in chicks with rickets.[219] In laying hens there is a high range of variation of the serum phosphatase which is not reduced by the administration of irradiated ergosterol. Plasma phosphatase is increased in rachitic children less than two years of age. Its continued rise may be prevented by the use of vitamin D.[220]

Morelle[221] studied the healing of experimental fractures in three groups of rats receiving respectively 1, 10, and 2 to 4 mg. of irradiated ergosterol per day. No effects were apparent before the twentieth day, but after that time the fracture lines were invisible in those receiving the medium dose, although they were still apparent in controls. After the thirtieth day, there was a dense callus in the treated animals and in the controls the disappearance of the fracture line had just begun. Heavy doses caused abnormally dense and exuberant callus formation. The conclusion of Grauer[222] from similar experiments was that therapeutic doses stimulate the osteogenic layer and favor repair. Overdoses stimulate the fibrous layer of the periosteum by decalcification of bones and retard repair. Fischer and Key,[223] however, are of the opinion that the addition of either calcium or vitamin D to the diet does not lessen the local atrophy of disuse or accelerate the union of bones.

Although some have expressed the view that the vitamin acts by stimulating the parathyroids, this is by no means generally conceded.[224] Comel[225] believed that after removal of the parathyroids life could be maintained indefinitely by giving vitamin D, but Lesné, Dubois and Simonnet[226] find that it does not serve as a substitute for the hormone.[227]

Dosage. As early as 1927, reports of the clinical efficacy of irradiated ergosterol began to appear.[228] The use of a preparation of irradiated ergosterol as a comparison standard for the assay of the antirachitic action was described by Coward and adopted by the British Pharmaceutical Society.[229] Its potency was such that a daily dose of not more than 0.1γ produced complete healing of rickets induced in rats under prescribed conditions. The unit of antirachitic potency was then defined as the amount of activity contained in 0.1γ of the standard preparation. The standard subsequently adopted by the Medical Research Council was prepared by freeing the irradiation product from alcohol, and dissolving it in pure unadulterated olive oil, the volume being adjusted to make a known concentra-

[217] Croxatio, H., *Compt. rend. soc. biol.*, **108**, 117 (1931); *Chem. Abs.*, **26**, 3009 (1932); see also Fischmann, C. F., *Arch. exptl. Zellforsch.*, **19**, 211 (1937); *Chem. Abs.*, **31**, 8618 (1937).

[218] Heymann, W., *Biochem. Z.*, **227**, 1 (1930); see also Bauer, W., Marble, A., and Claflin, D., *J. Clin. Investigation*, **11**, 21, 37, 47 (1932).

[219] Common, R. H., *J. Agr. Sci.*, **26**, 492 (1936); *Chem. Abs.*, **30**, 8327 (1936).

[220] Stearns, G., and Warweg, E., *Am. J. Diseases of Children*, **49**, 79 (1935); *Chem. Abs.*, **29**, 2581 (1935); Morris, N., Stevenson, M. M., Peden, O. D., and Small, J., *Arch. Diseases of Childhood*, **12**, 45 (1937). Compare earlier negative findings of Fabisch, W., *Biochem. Z.*, **254**, 158 (1932); *Chem. Abs.*, **27**, 525 (1933) and Rossi, A., and De Rienzo, A., *Boll. soc. ital. biol. sper.*, **8**, 719 (1933); *Chem. Abs.*, **29**, 2557 (1935).

[221] Morelle, J., *Rev. Belge Sci.*, **2**, 226 (1930); *Chem. Abs.*, **25**, 2463 (1931).

[222] Grauer, R. C., *Arch. Surgery*, **25**, 1035 (1932); *Chem. Abs.*, **27**, 1946 (1933).

[223] Fischer, F., and Key, J. A., *Archiv. Surgery*, **29**, 3112 (1934); *Chem. Abs.*, 28, 6796 (1934).

[224] Thomson, D. L., and Collip, J. B., *Physiol. Rev.*, **12**, 309 (1932).

[225] Comel, M., *Arch. Fisiol.*, **29**, 123 (1930); *Chem. Abs.*, **26**, 180 (1932).

[226] Lesné, E., Dubois, R., and Simonnet, H., *J. Physiol. Path. Gén.*, **30**, 65 (1932); *Chem. Abs.*, **26**, 4876 (1932).

[227] See also Popoviciu, G., and Nitzescu, I. I., *Z. ges. Exptl. Med.*, **81**, 656 (1932); *Chem. Abs.*, **27**, 4565 (1933); Asher, D. W., and Jones, J. H., *J. Biol. Chem.*, **100**, 333 (1933); Stacey, R. S., *Lancet*, **II**, 656 (1935); Deutsch, H., Reed, C. I., and Struck, H. C., *Am. J. Physiol.*, **117**, 1 (1936); Brougher, J. C., *Ibid.*, **86**, 538 (1928); Morgan, A. F., and Garrison, E. A., *J. Biol. Chem.*, **85**, 687 (1930); Mathieu, F., *Compt. rend. soc. biol.*, **114**, 1375 (1933); *Chem. Abs.*, **28**, 1744 (1933); Dale, H. H., Marble, A., and Marks, H. P., *Proc. Roy. Soc.*, **111B**, 522 (1932).

[228] Hess, A. F., *J. Am. Med. Assoc.*, **89**, 337 (1927); Schippers, J. C., *Nederland. Tijdschr. Geneesk.*, **72**, 3898 (1928); *Chem. Abs.*, **22**, 4154 (1928); Sobel, J., and Claman, I., *Arch. Ped.*, **46**, 1 (1929); *Chem. Abs.*, **23**, 1938 (1929).

[229] Coward, K. H., *Quart. J. Pharm.*, **1**, 27 (1928); *Chem. Abs.*, **22**, 4154 (1928); *Lancet*, **II**, 503 (1930).

tion in terms of the ergosterol used. Such solutions retained their activity unchanged for two years if maintained at or below 0°C.

In practice, cod-liver oil was checked against this standard and adjusted to contain a definite concentration of the vitamin in terms of the standard. Unfortunately, much confusion arose in regard to the strength of the cod-liver oil adopted as comparison standard. The system of the British Medical Research Council called for a cod-liver oil containing 100 units per cc. This was altered by the League of Nations to 100 units per gram, the strength adopted in the U. S. Pharmacopoeia in 1934. The Steenbock system used an oil standardized to contain 37 units per gram and the Holmes system (employed for a time by the American Drug Manufacturers Association) one with 350 units per gram. Still other systems have been used in other countries.[230]

The present vitamin D unit[231] is equivalent to 0.025γ of calciferol.

Bills[232] considers that the smallest dose which can be relied on to prevent rickets or to heal mild rickets in infants is about 3000 international units (I.U.) per day in the form of irradiated ergosterol or 1000 I.U. in the form of cod-liver oil. The Council on Pharmacy and Chemistry of the American Medical Association[233] adopted the name Viosterol to designate irradiated ergosterol and Viosterol in Oil to designate a preparation containing the substance dissolved in oil. The qualifying phrases 100 D, 5 D, etc. were added to the label to indicate the potency as a multiple of the potency of good cod-liver oil.

The successful use of large doses, 10 to 20 drops daily of viosterol, in late rickets was described by Shelling and Hopper.[234] Spence[235] found calciferol as effective as cod-liver oil or irradiated ergosterol in human rickets. One cc. of a solution containing 3000 units, administered daily, produced a maximum curative effect.

Recently, there has been much discussion as to the effects of variations in the calcium and phosphorus of the diet given during the administration of the vitamin, but this cannot be considered here.[236]

Toxic Effects. Hypervitaminosis D. About 1928, it became evident that irradiated ergosterol preparations may exert toxic effects.[237] Particularly dangerous properties were ascribed to the imported Vigantol.[238] After the administration of large quantities of this material to rats, Herzenberg[239] observed a necrosis in the smooth and striated muscles, followed by a deposition of calcium in the necrotic areas. The deposition of calcium was observed in the heart muscle and in elastic muscle fibers of blood vessel walls but the changes were different in character from those of arteriosclerosis. Schoenholz[240] found that pregnant rats which had received an overdose (10 mg. of Vigantol per day), lost their appetities and became sick. The fetuses were resorbed *in utero* or aborted. The live young were very small and usually died. Calcium deposits were observed

[230] See Bills, C. E., *Physiol. Rev.*, **15**, 1 (1935).
[231] *Quart. Bull. Health Org. League of Nations*, **3**, 428 (1934).
[232] Bills, C. E., *Physiol. Rev.*, **15**, 1 (1935).
[233] *J. Am. Med. Assoc.*, **93**, 693 (1929).
[234] Shelling, D. H., and Hopper, K. B., *Am. J. Diseases of Children*, **47**, 61 (1934).
[235] Spence, J. C., *Lancet*, **225**, 911 (1933); *Chem. Abs.*, **28**, 5503 (1934).
[236] See Bruce, H. M., and Callow, R. K., *Biochem. J.*, **28**, 512 (1934).
[237] Wurzinger, S., *Klin. Wochschr.*, **7**, 1859 (1928); *Chem. Abs.*, **24**, 3042 (1930); Reyher, P., and Walkoff, E., *Münch. Med. Wochschr.*, **75**, 1071 (1928); *Chem. Abs.*, **23**, 4728 (1929); Kreitmair, H., *Münch. Med. Wochschr.*, **75**, 637 (1928); Lasch, F., *Klin. Wochschr.*, **7**, 2148 (1928).
[238] Hess, A. F., and Lewis, J. M., *J. Am. Med. Assoc.*, **91**, 783 (1928).
[239] Herzenberg, H., *Beitr. Path. Anat.*, **82**, 27 (1929); *Chem. Abs.*, **23**, 4725 (1929); (Sclerosis in Man), Gerlach, W., *Münch. Med. Wochschr.*, **83**, 49 (1936).
[240] Schoenholz, L., *Klin. Wochschr.*, **8**, 1257 (1929); *Chem. Abs.*, **24**, 890 (1930).

in the livers of some of the mothers. A number of German workers observed involvement of the kidneys. These observations stimulated a great number of publications, of which but a few need be cited.[241]

A toxic calcification factor was defined[242] as the smallest amount which, given daily for a period of ten days, causes a mouse to lose 2.5 gm. in weight or to die. Mice receiving larger doses showed calcareous deposits in the kidneys. The ratio between the antirachitic rat dose and the mouse calcification factor was considered the therapeutic index of an irradiated ergosterol preparation.

It soon became evident that there were considerable differences between the antirachitic and toxic doses of variously irradiated preparations. With Vigantol, the margin of safety was very narrow.[243] The spectrographic study of the irradiation process soon made it apparent why this was the case. It was prepared according to a patent[244] which directed that the irradiation be continued until spectrographic observations indicated that there had been a maximum formation of a substance absorbing chiefly at 2480A. This is, as has been stated in a preceding section, now known to be toxisterol or substance 248, the overirradiation product. Subsequently it has been learned that D_2 and even the D_3 of cod-liver oil are also toxic in large doses. It is, however, evident that the formation of substance 248 should be avoided, since it is not only toxic but its formation occurs at the expense of that of the true antirachitic substance. The toxicity of calciferol in large doses was demonstrated by Askew, Bourdillon, Bruce, Callow, Philpot and Webster and by other research groups.[245]

At one time, Holtz and Schreiber[246] believed that the true vitamin when isolated would prove nontoxic and attempts were made to employ partition between immiscible solvents and various chemical procedures for separating the assumed toxic and antirachitic fractions. The failure of these attempts and the observation that D_1 had toxic properties led Windaus, Busse and Weidlich[247] to agree that the true vitamin possesses toxicity. It was found possible by chemical means to destroy the antirachitic activity without lessening the toxicity, but the converse was not possible. The English workers found that the ratio of the toxic dose in mice to the curative dose in rats is about 4000 to 1. The finding that D_2 has toxic properties proved[248] that Reiter had been in error in claiming that irradiation with wave-lengths longer than 2800A produces a non-toxic product.[249] It is, of course, true that the use of such long wave-lengths lessens the danger of the production of the toxic substance 248 by overirradiation. Whether or not tachysterol itself has toxic properties is not yet known, but its thermal decomposition products are highly toxic.[250]

[241] Bamberger and Spranger, *Deut. Med. Wochschr.*, **54**, 1116 (1928); Wiskott, A., *Münch. Med. Wochschr.*, **75**, 1445 (1928); Adam, A., *Klin. Wochschr.*, **7**, 1825 (1928); Degkwitz, R., *Münch. Med. Wochschr.*, **75**, 1631 (1928); Bamberger, Ph., *Deut. Med. Wochschr.*, **55**, 399 (1929); György, P., *Klin. Wochschr.*, **8**, 684 (1929); Putschar, W., *Z. Kinderheilk.*, **48**, 269 (1929); Klausner-Cronheim, I., *Deut. Med. Wochschr.*, **56**, 1566 (1930).
[242] Holtz, F., Lacquer, F., Kreitmair, H., and Moll, T., *Biochem. Z.*, **237**, 247 (1931); *Münch. Med. Wochschr.*, **78**, 1688 (1931); *Chem. Abs.*, **26**, 3011 (1932).
[243] Göttche, O., and Kellner, B., *Arch. Kinderheilk.*, **94**, 129 (1931).
[244] British P. 296,093, Nov. 15, 1928, to I. G. Farbenind. A.-G.
[245] Askew, F. A., Bourdillon, R. B., Bruce, H. M., Callow, R. K. Philpot, J., and Webster, T. A., *Proc. Roy. Soc.*, **109**, 488 (1932); Dale, H. H., Marble, A., and Marks, H. P., *Ibid.*, **111B**, 522 (1932); Gough, J., Duguid, J. B., and Davies, D. R., *Brit. J. Exptl. Path.*, **14**, 137 (1933); Harris, L. J., and Moore, T., *Biochem. J.*, **22**, 1461 (1928); Harris, L. J., and Innes, J., *Ibid.*, **25**, 367 (1931).
[246] Holtz, F., and Schreiber, E., *Z. physiol. Chem.*, **191**, 3 (1930); Windaus, A., and Auhagen, E., *Z. physiol. Chem.*, **196**, 108 (1930); **197**, 167 (1931).
[247] Windaus, A., Busse, P., and Weidlich, G., *Z. physiol. Chem.*, **202**, 246 (1931).
[248] Laquer, F., *Klin. Woch.*, **10**, 1072 (1931); *Deut. Med. Wochschr.*, **57**, 243 (1931); *Chem. Abs.*, **26**, 3010 (1932).
[249] Reiter, T., *Naturwiss.*, **17**, 876 (1929); Kisch, E., and Reiter, T., *Deut. med. Wochschr.*, **56**, 2034 (1930); *Chem. Abs.*, **25**, 4918 (1931).
[250] Windaus, A., and Lüttringhaus, A., *Deut. Med. Wochschr.*, **58**, 1669 (1932).

A review of the nature of the toxic effects of D_2 and of cod-liver oil has been given by Agduhr, Blix and Vahlquist.[251] A fatal case in a child has been described by Thatcher.[252] Ham and Lewis [253] found that large doses of vitamin D given to normal young rats interfered with the processes of bone calcification and actually produced rachitic lesions. They suggested that the action may be to increase the attraction of the blood for calcium. Baumgartner, King and Page [254] found overdoses to produce softening of the skeletal framework of rabbits and a low bone phosphatase. The ratio of calcium to phosphorus in the bone is not affected according to Kramer, Shear and McKenzie.[255]

That the hypercalcemia alone is not responsible for the toxic effects, since it is compatible with life, is the belief of Taylor, Weld and Sykes.[256]

It is generally found that the hypercalcemia may be produced even on a low calcium diet, some claiming at the expense of the bones.[257]

Daily subcutaneous injections of irradiated ergosterol produce local calcification in the subcutaneous tissues, according to von Brand and Holtz. Calcification in the kidneys is less than after the oral administration of the same doses.[258] In general, after a toxic state with calcium deposition has been reached, the discontinuance of the administration of the vitamin leads to a reversal of the process and the repair of the lesions.[259] Both human subjects and dogs usually survive 20,000 to 30,000 units per kg. per day for indefinite periods. In rats, it is agreed by many that 10,000 times the minimum antirachitic dose is not lethal and several say not harmful.[260] Bills and Wirick [261] found 1000 times overdosage to be just perceptibly harmful, 4000 times overdosage to be definitely injurious and 40,000 times overdosage strongly toxic. Harris and Moore [262] found a 100,000 times overdosage rapidly fatal, and Collazo, Rubino and Varela Fuentes [263] found 50,000 times the normal dose fatal within six weeks. Young rats and puppies remained normal with doses up to 1000 times the minimal effective dose according to Cartland, Speer and Heyl.[264]

[251] Agduhr, E., Blix, G., and Vahlquist, B., *Uppsala Läkäreforeningen*, **39**, 304; **40**, 183; *Chem. Abs.*, **29**, 8145 (1935); for the pathologic anatomy, Duguid, J. B., *Lancet*, **II**, 983 (1930); Barr, D. P., *Physiol. Rev.*, **12**, 593 (1932); Nitzescu, I. I., and Bratiano, S., *Compt. rend. soc. biol.*, **121**, 1533 (1936).

[252] Thatcher, L., *Edinburgh Med. J.*, **38**, 457 (1931); *Chem. Abs.*, **25**, 5446 (1931).

[253] Ham, A. W., and Lewis, M. D., *Brit. J. Exptl. Path.*, **15**, 228 (1934); *Chem. Abs.*, **28**, 7301 (1934).

[254] Baumgartner, L., King, E. J., and Page, I. H., *Biochem. Z.*, **213**, 170 (1929); *Chem. Abs.*, **24**, 403 (1930).

[255] Kramer, B., Shear, M., and McKenzie, M. R., *J. Biol. Chem.*, **82**, 555 (1929).

[256] Taylor, N. B., Weld, C. B., and Sykes, J. F., *Brit. J. Exptl. Path.*, **17**, 104 (1936). For the effects of small doses of concentrated preparations on the blood calcium and phosphorus of monkeys, see Cowdry, E. V., and Scott, G. H., *Arch. Path.*, **22**, 1 (1936).

[257] Soeur, R., *Arch. Int. Med. Exptl.*, **6**, 365 (1931); *Chem. Abs.*, **25**, 4588 (1931); Jones, J. H., and Rapoport, M., *J. Biol. Chem.*, **93**, 153 (1931); Jones, J. H., and Robson, G. M., *Ibid.*, **91**, 43 (1931); Thoenes, F., *Jahrbuch Kinderheilk.*, **126**, 348 (1929); *Chem. Abs.*, **26**, 501 (1932); *Jahrb. Kinderheilk.*, **129**, 171 (1930); Jones, J. H., Rapoport, M., and Hodes, H. L., *J. Biol. Chem.*, **89**, 647 (1930); Wiskott, A., *Z. Kinderheilk.*, **49**, 79 (1930); *Chem. Abs.*, **26**, 4362 (1932); Kern, R., Montgomery, M. E., and Still, E. U., *J. Biol. Chem.*, **93**, 365 (1931); Cole, V. V., and Koch, F. C., *Ibid.*, **94**, 263 (1931); Hess, A. F., Benjamin, H., and Gross, J., *Ibid.*, **94**, 1 (1931); Pozzi, L., and Preto, E., *Biochem. terap. sper.*, **18**, 397 (1932); *Chem. Abs.*, **27**, 1667 (1933); Kletzien, S. W. F., Templin, V. M., Steenbock, H., and Thomas, B. H., *J. Biol. Chem.*, **97**, 265 (1932); von Euler, H., and Rydbom, M., *Biochem. Z.*, **249**, 141 (1932); Popoviciu, G., *Jahrb. Kinderheilk.*, **132**, 286 (1931); *Chem. Abs.*, **26**, 3013 (1932).

[258] von Brand, T., and Holtz, F., *Z. physiol. Chem.*, **195**, 241 (1931).

[259] Steck, I. E., Deutsch, H., Reed, C. I., and Struck, H. D., *Ann. Internal Med.*, **10**, 951 (1937); von Brand, T., and Holtz, F., *Z. physiol. Chem.*, **185**, 217 (1929); for storage after massive doses, see Heymann, W., *J. Biol. Chem.*, **118**, 371 (1937).

[260] Rosenheim, O., and Webster, T. A., *Biochem. J.*, **21**, 389 (1927); Light, R. F., Miller, G. E., and Frey, C. N., *J. Biol. Chem.*, **84**, 487 (1929).

[261] Bills, C. E., and Wirick, A. M., *J. Biol. Chem.*, **86**, 117 (1930).

[262] Harris, L. J., and Moore, T., *Biochem. J.*, **22**, 1461 (1928).

[263] Collazo, J. A., Rubino, P., and Varela Fuentes, B., *Biochem. Z.*, **204**, 347 (1929).

[264] Cartland, G. F., Speer, J. H., and Heyl, F. W., *J. Pharmacol.*, **36**, 619 (1929); *Chem. Abs.*, **24**, 404 (1930).

In the human, no ill effects were noted with 20 to 50 times the ordinary doses by Hess, Poncher, Dale and Klein,[265] other than a tendency to constipation and colic. In patients with tetany no toxic effects were noted with 300 times overdosage.[266] Bills believes that in man toxic effects begin to appear at 200 times the ordinary dose, that is when 600,000 I.U. of properly irradiated ergosterol are given daily over several weeks. Rappaport and Reed gave 3 cc. per day of a concentrated solution 10,000 D, and known to contain a million I.U. per gram. Although this was 2,760,000 I.U. or 920 times the ordinary therapeutic dose, no serious poisoning was produced. The largest recorded human dose, 6000 times the ordinary dose, produced hypercalcemia, but no pathological calcification of tissues.[267]

Excessive doses of fish-liver oils are less apt to produce hypervitaminosis.[268]

Relation to Tuberculosis. Because of the remedial effects of ultraviolet irradiation of tuberculous patients, many studies have been made of the effects of vitamin D in that disease in order to determine whether its action may account for the effects of general irradiation. The calcifying action of the vitamin might be expected to be of value in the treatment of the disease.[269] Simonnet and Tanret [270] found large doses of irradiated ergosterol to cause a notable increase in pulmonary calcification in tuberculous rabbits. In chronic tuberculosis the evolution of tubercles was checked. Pfannstiel and Scharlau [271] reported somewhat less favorable results on rabbits primarily infected but found favorable results in somewhat immunized rabbits. Meersseman and Tricault [272] found tuberculous guinea pigs given vitamin D to live longer and have less severe lesions than the controls. They also reported improvement in eleven human patients. Spies and Berryhill [273] sugested a diet high in vitamin D for patients with intraperitoneal tuberculosis. Long [274] agreed that viosterol by mouth increases calcification in experimental tuberculosis.

Many of those who obtained negative results did not employ massive doses.[275] Haubold [276] even claimed that small doses stimulated the disease in guinea pigs. Spies and Walker [277] obtained less distinct results in experimental avian than in the bovine tuberculosis. Poncher and Gasul [278] drew no conclusions as to the effect of moderately large doses in tuberculous children, but believed the secondary effects of such therapy unfavorable. Negative results in intestinal

[265] Hess, J. H., Poncher, H. G., Dale, M. L., and Klein, R. I., *J. Am. Med. Assoc.*, **95**, 316 (1930).

[266] Reed, C. I., and Seed, L., *Endocrinology*, **17**, 136 (1933); but see Rappaport, B. Z., and Reed, C. I., *J. Am. Med. Assoc.*, **101**, 105 (1933).

[267] Spies, T. D., and Hanzal, R. F., *Proc. Soc. Exptl. Biol. Med.*, **31**, 747 (1935).

[268] Morgan, A. F., Kimmel, L., and Hawkins, N. C., *J. Biol. Chem.*, **120**, 85 (1937); Martinelli, A., *Probl. alimentare*, **4**, 1 (1934); *Ber. ges. Physiol. exptl. Pharmakol.*, **87**, 82; *Chem. Abs.*, **31**, 7951 (1937).

[269] The subject has been reviewed by Guilbert, G. D., *Med. Bull. Veterans' Admin.*, **10**, 141 (1934). See also Kaminsky, J., and Davidson, D., *Am. Rev. Tuberc.*, **22**, 48 (1930); Hildebrand, C. J., *Ibid.* **22**, 53 (1930).

[270] Simonnet, H., and Tanret, G., *Compt. rend.*, **190**, 1526 (1930).

[271] Pfannstiel, W., and Scharlau, B., *Beitr. klin. Tuberk.*, **73**, 351 (1930); *Chem. Abs.*, **25**, 2172 (1931).

[272] Meersseman, F., and Tricault, G., *Semana Med. Buenos Aires*, **I**, 595 (1931); *Chem. Abs.*, **25**, 2485 (1931).

[273] Spies, T., and Berryhill, W. R., *Am. Rev. Tuberc.* **26**, 275 (1932); *Chem. Abs.*, **27**, 775 (1933).

[274] Long, E. R., *Proc. Soc. Exptl. Biol. Med.*, **30**, 1090 (1933).

[275] Simonnet, H., and Tanret, G., *Presse Med.*, **39**, 932 (1931); Grayzel, H. G., Shear, M. J., and Kramer, B., *Am. Rev. Tuberc.*, **24**, 106 (1931); Kaminsky, J., and Davidson, D. L., *Ibid.*, **24**, 483 (1931); Freund, R., *Beitr. klin. Tuberk.*, **78**, 666 (1931); *Chem. Abs.*, **26**, 6012 (1932); Zeyland, J., and Piasecka-Zeyland, E., *Tubercle*, **17**, 198 (1936); Crimm, P. D., and Strayer, J. W. *Ann. Int. Med.*, **9**, 1393 (1936); Loewen, D. F., and Oatway, W. H., *J. Am. Rev. Tuber*, **33**, 733 (1936).

[276] Haubold, H., *Z. Tuberk.*, **67**, 247 (1933); *Chem. Abs.*, **27**, 5100 (1933).

[277] Spies, T., and Walker, T. T., *Am. Rev. Tuberc.*, **64**, 23, 65 (1931); **74**, 723 (1931).

[278] Poncher, H. G., and Gasul, B. M., *Am. Rev. Tuberc.*, **30**, 358 (1934); *Chem. Abs.*, **28**, 7303 (1934).

tuberculosis have been reported by Steinbach and Rosenblatt.[279] More or less favorable evidence for the use of irradiated ergosterol in tuberculosis is also to be found in the following papers.[280]

DeJust[281] reported the cure of two cases of tuberculous osteitis with fistulas after a score of instillations of viosterol into the fistulas.

Other Effects. Mellanby[282] called attention to the fact that exposure of puppies on a moderately defective diet to the rays of a mercury arc had a beneficial effect upon the calcification and structure of the teeth. If the diets were very bad, however, the calcification became poorer on irradiation. Later, Mellanby and Pattison[283] found a cereal-free diet rich in calcium and vitamin D to almost eliminate the initiation and spread of caries in children. Similar favorable reports are due to Agnew, Agnew and Tisdall[284] and others.[285] Little evidence for a protective action of the vitamin against caries could be found, however, by Rosebury and Karshan[286] or Shelling and Anderson.[287] Blackberg and Berke[288] noted a relationship in dogs between a deficiency in the vitamin and certain changes in the pulp, enamel and dentine which are poorly calcified.[289]

The use of irradiation in the treatment of hay fever and asthma finds some confirmation in the work of Rappaport, Reed, Hathaway and Struck,[290] who observed that Viosterol, in large doses, combined with pollen injections is more effective than either alone. Rappaport and Reed[291] found Viosterol without effect in three cases of infectious asthma and two of urticaria, but it did protect six hay fever patients. Favorable effects of vitamin D on eczema have been reported.[292]

The ability of ergosterol to sensitize the pneumococcus to lysis by saponin is destroyed by irradiation.[293]

Viosterol has neither antiseptic nor bactericidal properties.[294] Greene[295] in an extensive study, was unable to detect any effect of a deficiency in vitamin D upon the ability of animals to produce antibodies or to resist infections. This is also the conclusion of Hess.[296]

Notwithstanding these generally negative results, there have been papers purporting to show that D increases the resistance to infection. Robertson and Ross[297] found rachitic rats receiving *B. enteriditis* orally showed a 5 per cent survival when the diet contained non-irradiated and 30 per cent survival when it contained irradiated whole wheat. Similar effects also were described as due to the direct irradiation of the rat through Vitaglass. Koboshi[298] found subcutaneous injections of staphylococci to produce more serious effects in rats deprived of vitamins A and D than in normal animals. Doses of Vigantol prevented the appearance of abscesses. Choun[299] believed a high-vitamin diet to increase the resistance of guinea pigs to diphtheria. Pfannenstiehl[300] noted a decreased germicidal power of the blood for typhoid organisms in D avitaminosis. Kemmler[301] found skin wounds to heal more rapidly when an irradiated ergosterol solution was applied directly. Pritchett[302] believed the resistance of mice on a normal diet to infection with paratyphoid bacillus or mouse typhoid bacillus to be increased by the addition of butter fat, cod-liver oil or by the use of irradiated milk.

It has been suggested that viosterol may be of value in the treatment of lead poisoning, since in cats large doses increase the excretion of that metal.[303]

Irradiated ergosterol is also asserted to increase the thrombocytes in blood and to reduce the coagulation time.[304] It, as well as ultraviolet irradiation, tends to produce an increase in the fibrinogen and a decrease in the antithrombin content of the blood of newborn infants.[305] Leopold, Bernhard and Tow[306] report the lipids of the blood of children to be increased after ultraviolet irradiation, although the lipoid-phosphorus content is not changed. Nakae,[307] finds in rabbits that the daily administration of 0.1 to 1.5 cc. of irradiated ergosterol preparations decreases the serum cholesterol by about 40% in a month. Blood catalase is increased by small doses but decreased by an excess of vitamin D, according to Jusatz.[308] Feeding moderate amounts does not affect the glutathione level in the blood, but after toxic doses, although the number of red cells is increased, each cell has a reduced glutathione content.[309]

It seems well established that metabolism is increased by vitamin D. Handovsky[310] found irradiated ergosterol to increase the oxygen consumption of

[279] Steinbach, M. M., and Rosenblatt, M. B., *Am. Rev. Tuberc.*, **31**, 35 (1935); *Chem. Abs.*, **29**, 4410 (1935).

[280] Levaditi, C., and Li, Y. P., *Compt. rend. soc. biol.*, **106**, 169 (1931); *Chem. Abs.*, **25**, 3382 (1931); Policard, A., Ravault, P., and Barral, P., *Compt. rend. soc. biol.*, **104**, 633 (1930); *Chem. Abs.*, **25**, 4916 (1931); Pachioli, R., and Mengoli, V., *Bol. Soc. Ital. Biol. Sper.*, **6**, 448 (1931); *Chem. Abs.*, **26**, 764 (1932); Haubold, H., *Beitr. Path. Anat.*, **89**, 633 (1932); *Chem. Abs.*, **26**, 5660 (1932); Loewy, A., and Grüninger, W., *Z. Tuberk.*, **61**, 317 (1931); *Chem. Abs.*, **26**, 6011 (1932); Crimm, P. D., *Am. Rev. Tuberc.*, **26**, 112 (1932); Black, W. C., Desavitsch, E. C., Trevorrow, V. E., and Lewis, R. C., *Ibid.*, **28**, 699 (1933).

[281] DeJust, L. H., *Rev. actinologie physiotherap.*, **6**, 1 (1931); *Chem. Abs.*, **26**, 2793 (1932).

[282] Mellanby, E., *Brit. Dental J.*, **45**, 545 (1924).

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[286] Rosebury, T., and Karshan, M., *Arch. Path.*, **20**, 697 (1935).

[287] Shelling, D. H., and Anderson, G. M., *J. Am. Dental Assoc.*, **23**, 840 (1936); *Chem. Abs.*, **30**, 5624 (1936).

[288] Blackberg, S. N., and Berke, J. D., *J. Dental Res.*, **12**, 349 (1932); *Chem. Abs.*, **26**, 5129 (1932).

[289] See also Templin, V. M., and Steenbock, H., *J. Biol. Chem.*, **100**, 217 (1933); Schour, I., and Ham, A. W., *Arch. Path.*, **17**, 22 (1934); *Chem. Abs.*, **28**, 2762 (1934).

[290] Rappaport, B. Z., Reed, C. I., Hathaway, M. L., and Struck, H. C., *J. Allergy*, **5**, 541 (1934); *Chem. Abs.*, **28**, 7361 (1934).

[291] Rappaport, B. Z., and Reed, C. I., *J. Am. Med. Assoc.*, **101**, 105 (1933).

[292] Comel, M., *Giorn. ital. dermat.*, **76**, 89 (1935); *Ber. ges. Physiol. exptl. Pharmakol.*, **88**, 59; *Chem. Abs.*, **31**, 8629 (1937).

[293] Klein, S. J., *J. Bacteriol.*, **26**, 215 (1933).

[294] Montgomery, B. E., *Proc. Soc. Exptl. Biol. Med.*, **28**, 481 (1930).

[295] Greene, M. R., *Am. J. Hyg.*, **17**, 60 (1933); *Chem. Abs.*, **27**, 1661 (1933).

[296] Hess, A. F., *New England J. Med.*, **207**, 367 (1932). See, however, Holm, R., *Z. Immunitäts*, **82**, 479 (1934); *Chem. Abs.*, **28**, 7346 (1934). For a general review, see Clausen, S. W., *Physiol. Rev.*, **14**, 309 (1934); Robertson, E. C., *Medicine*, **13**, 123 (1934).

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[298] Koboshi, S., *J. Chosen Med. Assoc.*, **23**, 39 (1933); *Chem. Abs.*, **28**, 4453 (1934).

[299] Choun, C. K., *Z. Immunitäts.*, **81**, 432 (1934); *Chem. Abs.*, **28**, 5505 (1934).

[300] Pfannenstiehl, W., *Sitzsber. Ges. Beförder ges. Naturw. Marburg*, **67**, 71 (1932); *Chem. Abs.*, **28**, 5507 (1934).

[301] Kemmler, H., *Mitt. Grenzgeb. Med. Chir.*, **43**, 453 (1934); *Chem. Abs.*, **29**, 5927 (1935).

[302] Pritchett, I. W., *J. Exptl. Med.*, **46**, 557 (1927).

[303] Flinn, F. B., and Smith, A. R., *J. Ind. Hyg.*, **15**, 156 (1933); *Chem. Abs.*, **27**, 3529 (1933).

[304] Phillips, R. A., Robertson, D. F., Corson, W. C., and Irwin, G. F., *Ann. Int. Med.*, **4**, 1134 (1931); *Chem. Abs.*, **25**, 5210 (1931).

[305] Sanford, H. N., Gasteyer, T. H., and Wyat, L., *Am. J. Diseases of Children*, **43**, 566 (1932); *Chem. Abs.*, **26**, 3560 (1932); Babasaki, Y., *Folia Pharmacol. Japon.*, **14**, 1 (1932); *Chem. Abs.*, **26**, 4100 (1932).

[306] Leopold, J. S., Bernhard, A., and Tow, A., *Am. J. Diseases of Children*, **43**, 882 (1932); *Chem. Abs.*, **26**, 4350 (1932).

[307] Nakae, R., *Nagoya J. Med. Sci.*, **7**, 88 (1933); *Chem. Abs.*, **28**, 3457 (1934).

[308] Jusatz, H. J., *Klin. Wochschr.*, **11**, 1501 (1932); *Chem. Abs.*, **27**, 1030 (1933).

[309] Hesse, H., *Biochem. Z.*, **268**, 304 (1934).

[310] Handovsky, H., *Arch. Exptl. Path. Pharmakol.*, **159**, 383 (1931); *Chem. Abs.*, **25**, 4053 (1931).

liver sections *in vitro*. Dhar[311] has suggested that vitamin D may be essential to the proper oxidation of fats in the body. In infants with rickets or tetany, Nitschke and Schneider[312] observed a lowered metabolic rate, which could be made to rise by giving the vitamin. Reed, Thacker, Dillman and Welch[313] found large doses of irradiated ergosterol to increase the metabolic rate of normal dogs. Landelium and Ljungkvist[314] have confirmed the ability of the vitamin to increase the depressed oxygen consumption of rachitic rats. Reed[315] found the administration of 20,000 to 552,000 I.U. daily, as Viosterol, to rats in two to six days caused first a marked increase in the metabolic rate, followed by a decrease and an irregular return to normal. On the other hand, Massaroli,[316] using the metadinitrobenzene method, found irradiated ergosterol to slow down the oxidation-reduction processes of the tissues. An increase may be observed in the respiration of the skin, according to Presnell.[317] It is said that the injection of irradiated (but not of unirradiated) ergosterol into the gall bladder of guinea pigs causes adenoid growths.[318]

It has been stated that irradiated cholesterol accelerates alcoholic fermentation in brewing, although non-irradiated cholesterol inhibits it.[319]

[311] Dhar, N. R., *J. Phys. Chem.*, **36**, 1846 (1932).
[312] Nitschke, A., and Schneider, M., *Z. Kinderheilk.*, **54**, 1 (1932); *Chem. Abs.*, **27**, 5399 (1933).
[313] Reed, C. I., Thacker, E. A., Dillman, L. M., and Welch, J. W., *J. Nutrition*, **6**, 355 (1933); *Chem. Abs.*, **27**, 5785 (1933).
[314] Landelium, E., and Ljungkvist, G., *Skand. Arch. Physiol.*, **68**, 252 (1934); *Chem. Abs.*, **28**, 4460 (1934).
[315] Reed, C. I., *Proc. Exptl. Biol. Med.*, **32**, 274 (1934).
[316] Massaroli, P., *Riv. pat. Sper.*, **10**, 1 (1933); *Chem. Abs.*, **28**, 3457 (1934).
[317] Presnell, A. K., *J. Biol. Chem.*, **121**, 5 (1937).
[318] Schmidt, H. O., *Z. Krebsforsch.*, **45**, 335 (1937); *Chem. Abs.*, **31**, 5874 (1937).
[319] De Fazi, R., and Pirrone, F., *Ann. Chim. Applicata*, **21**, 419 (1931); *Chem. Abs.*, **26**, 799 (1932); Pirrone, F., *Ann. Chim. Applicata*, **22**, 731 (1932); *Chem. Abs.*, **27**, 1916 (1933); Mameli, E., and Mossini, A., *Giorn. Chim. Ind. Applicata*, **16**, 377 (1934); *Chem. Abs.*, **28**, 7415 (1934).

Chapter 40

Commercial Production of Vitamin D

Rickets is now recognized to be an extremely widespread disease, its incidence being as high as 50 to 75 per cent. This is because milk, the chief food of the infant, is relatively low in antirachitic potency. Eggs and fish are practically the only foods which contain large amounts of the necessary food factor. Vegetables are entirely lacking in it.[1] For this reason, the discoveries described in the preceding chapters quickly found application in the preparation of infant foods, pharmaceutical products and in improving the dietetic value of milk. In the preparation of poultry foods, the various methods of introduction of the vitamin have been of great economic importance.

Notwithstanding the fact that the process of irradiation of foodstuffs was discovered in the United States, its widespread adoption, at least in the case of dried milk and the production of pharmaceutical solutions containing irradiated sterols, seems to have come about first in Germany, where György reported on the value of irradiated milk as early as 1926. The earliest commercial milk irradiation was conducted in Frankfurt by Scheer and in Basel by Wieland.[2] Irradiated Dryco has been manufactured in the United States since about 1927: Steenbock applied for a patent on June 30, 1924, and this was issued in the United States[3] and assigned to the University of Wisconsin Alumni Research Foundation. By 1929, this foundation had licensed five drug manufacturers to produce irradiated sterol preparations.[4] By November, 1929, the American Medical Association had approved the name Viosterol for such preparations. At about this time, licenses were also granted for the irradiation of milk and various cereal preparations. In England, a Steenbock patent[5] made mention of the possibility of harmful overirradiation and stated that this could be avoided by limiting the time of exposure. The patent also included the separation of non-saponifiable lipids from fats either before or after the irradiation and their incorporation into foods. This included the preparation and irradiation of sterols and their esters obtained from such plant materials as yeast, molds, mushrooms, ergot, various seeds and straw, as well as from brain and other animal sources. In other U. S. Patents,[6] he described the irradiation of cereals or solid cereal products to a regulated degree to develop antirachitic properties without subsequent injury to either these properties or to the palatability, by strictly limiting the time.

There are a number of other patents dealing with irradiation processes. Tillisch,[7] claimed that irradiation of oils and fats produced, in addition to the antirachitic vitamin,

[1] Hess, A. F., "Rickets, including Osteomalacia and Tetany," p. 102, Philadelphia, Lea and Febinger, 1929.
[2] See also György, P., *Klin. Wochschr.*, **5**, 747 (1926); **4**, 1118 (1925).
[3] Steenbock, H., U. S. P. 1,680,818, Aug. 14, 1928, to Wisconsin Alumni Research Foundation.
[4] *Drug Markets*, **24**, 347 (1929).
[5] Steenbock, H., British P. 236,197, June 30, 1924; *J. Soc. Chem. Ind. Suppl.* **B**, 735 (1925); 314,942, July 5, 1928; *Chem. Abs.*, **24**, 1411 (1930).
[6] Steenbock, H., U. S. P. 1,871,135-6, Aug. 9, 1932, to Wisconsin Alumni Research Foundation; *Chem. Abs.*, **26**, 5675 (1932); German P. 605,960, Nov. 22, 1934; *Chem. Abs.*, **29**, 1862 (1935).
[7] Tillisch, H. C. E., British P. 270,296, April 28, 1926; *Chem. Abs.*, **22**, 1415 (1928).

the fat-soluble A if oxygen was excluded. This is now known not to be possible. The harmful effects of ozone were eliminated through the use of a calcspar filter in the method of Heinemann,[8] and Scholl [9] attained the same objective when he displaced the air from an irradiated liquid by the passage of an inert gas. Stamsö [10] increased the antirachitic potency of food oils, such as peanut oil, intended for a butter substitute, by irradiating it in thin layers with the exclusion of air, or by immersing lamps in the flowing liquid for not more than an hour. This was reduced to ten minutes in a later patent.[11] In other patents, there were many indefinite claims for the improvement of food products, without particular mention of the development of antirachitic potency, although this was undoubtedly the objective intended; the claims related to various details of the methods employed. Pacini [12] used rays other than those in the ultraviolet range, particularly infrared rays, or, in another patent,[13] rays longer than 3022A for the treatment of many substances such as bacilli, molds, sarcoma tissue, and ergot, said to contain a growth vitamin.

During ultraviolet irradiation of foodstuffs, Ried [14] employed a simultaneous irradiation either with x-rays or with wave-lengths longer than ultraviolet. Kelly [15] similarly proposed the simultaneous or subsequent application of cathode rays. The use of the latter alone was claimed by Knudson.[16] Sperti[17] claimed the use of soft x-rays.

Perino [18] described the use of an alkali monohydrogen phosphate solution in conjunction with the ultraviolet irradiation of various types of vegetable material.

Another type of patent covered the use of only restricted wave-length regions within the ultraviolet range in order to control the processes in such a manner as to avoid the accumulation of undesirable products or the destruction of the vitamin once it had formed. Thus, Sperti, Withrow, Norris and Schneider [19] described a process for simultaneously increasing the vitamin content and destroying bacteria in which foods are irradiated with ultraviolet light with the exclusion, by suitable filters, of those shorter wave-lengths which are harmful to the taste, smell and color of the food. Chesney [20] places the threshold for destructive effects in the irradiation of foods at about 2900A and avoids the action of shorter wavelengths by employing concentrated sunlight or skyshine. Bills [21] described an apparatus for exposing materials on a belt conveyor to sunlight filtered through a covering material such as Cellophane which is transparent to ultraviolet rays.

Reiter [22] used only radiations longer than 2800A in irradiating substances containing ergosterol to avoid the formation of toxic products. It is now recognized that this cannot be accomplished since D_2 itself has toxic properties, but the

[8] Heinemann, F., German P. 530,877, Nov. 4, 1926; *Chem. Abs.*, **26**, 221 (1932).

[9] Scholl, H., French P. 646,792, Dec. 28, 1927; *Chem. Abs.*, **23**, 2106 (1929); British P. 283,472, Jan. 9, 1928; *Chem. Abs.*, **22**, 4015 (1928); Canadian P. 285,853, Dec. 25, 1928; *Chem. Abs.*, **23**, 1231, 2330 (1929).

[10] Stamsö, K. K., British P. 246,473, Jan. 26, 1925; *Chem. Abs.*, **21**, 465 (1927).

[11] Stamsö, K. K., Swedish P. 72,502, Aug. 25, 1931; 72, 613, Sept. 8, 1931; *Chem. Abs.*, **27**, 3294 (1933).

[12] Pacini, A. J., British P. 296,053, Aug. 24, 1927; *Chem. Abs.*, **23**, 2252 (1929).

[13] Pacini, A. J., U. S. P. 1,681,120, Aug. 14, 1928, to C. N. Richter; *Chem. Abs.*, **22**, 3737 (1928).

[14] Ried, O., Austrian P. 121,657, Oct. 13, 1930; *Chem. Abs.*, **25**, 3130 (1931); see also for the preservation of foods in this way, the Fromray Co., British P. 325,824, *Chem. Abs.*, **24**, 3952 (1930); German P. 551,290.

[15] Kelly, T. D., British P. 293,255, Nov. 28, 1927; *Chem. Abs.*, **23**, 1698 (1929).

[16] Knudson, A., British P. 292,926, June 24, 1927; *Chem. Abs.*, **23**, 1446 (1929).

[17] Sperti, G., U. S. P. 1,982,028, Nov. 27, 1934, General Development Laboratories, Inc.; *Chem. Abs.*, **29**, 517 (1935).

[18] Perino, J., British P. 279,487, Oct. 20, 1926; *Chem. Abs.*, **22**, 2799 (1928); German P. 535,411; U. S. P. 1,754,434, April 15, 1930.

[19] Sperti, G., Withrow, R., Norris, R. ,and Schneider ,H., U. S. P. 1,982,029, Nov. 27, 1934, to General Development Laboratories, Inc., *Chem. Abs.*, **29**, 517 (1935). There is now available a vegetable oil solution of ergosterol prepared in this manner containing 10,000 units per gram. Rider, T., Sperti, G., Goode, P., and Cassidy, H., *J. Am. Med. Assoc.*, **106**, 452 (1936).

[20] Chesney, J. W. D., U. S. P. 1,704,173; *Chem. Abs.*, **23**, 1967 (1929); British P. 310,802, April 30, 1928.

[21] Bills, C. E., U. S. P. 1,877,382, Sept. 13, 1932; *Chem. Abs.*, **27**, 4 (1933).

[22] Reiter, T., French P. 697,367, Jan. 30, 1930; *Chem. Abs.*, **25**, 3131 (1931); British P. 342,500, Jan. 17, 1930.

formation of other inert toxic substances can be lessened. Most of the patents dealing with the use of filtered radiations were applied for before or shortly after the appearance of the work of Reerink and van Wijk, discussed in the preceding chapter. A study of this will aid in the evaluation of claims for the action of specific wave-lengths. Reiter's claims were in part based upon his observation [23] that, in the irradiation of milk, it is the wave-lengths between 2400 and 2800A which cause the undesirable changes in odor and taste.[24]

The Philips Gloeilampenfabriken [25] proposed to increase the efficiency by filtering out wave-lengths shorter than 2700A by the use of a 10-mm. layer of a 5 per cent benzene solution, or *p*-xylene.

Campsie [26] eliminated infrared rays and used a cold quartz lamp giving chiefly the band 2537-2540A, the resonance lines of mercury, radiations which most authorities would agree would have to be very carefully limited in their application if destruction of the antirachitic substance is to be avoided.

The use of the carbon arc for irradiating foods was described by Chaney.[27] The formation of ozone which gives off-flavor, is particularly avoided by the use of electrodes [28] containing added iron or aluminum so that the energy emitted will have a high proportion of wave-lengths between 2000 and 3000A, with only a negligible portion shorter than 2000A.

It is not possible to discuss in detail the many patents dealing with the structural features of irradiation apparatus.[29]

Shumway [30] removes the husk or skin from a cereal such as wheat, corn, oats, rye, barley or rice, and separates any pulverulent material, after which the whole cereal kernels are irradiated. Dorcas [31] described the apparatus commonly used for irradiating such foods. A thin layer of the product an eighth of an inch deep flows on a moving belt before an ultraviolet lamp.

Jaeger [32] described a therapeutic product prepared by irradiating dry banana meal in thin layers.

Berndt and Creighton [33] treat an opaque food substance at rest by ultraviolet rays only long enough to render a fraction of it antirachitic. This is then mixed with the untreated portion, again irradiated, the mixing and irradiation processes being alternately repeated, the total treatment received during the exposures of the fractions being less than the time required to impart undesirable properties to any portion.

[23] Reiter, T., *Naturwiss.*, **17**, 876 (1929); Kisch, E., and Reiter, T., *Strahlentherapie*, **39**, 452 (1930-31); Genin, G., [*Lait*, **17**, 47 (1937); *Chem. Abs.*, **31**, 7494 (1937)] avoids rays less than 2600A.

[24] See also Weckel, K. G., Jackson, H. C., Haman, R., and Steenbock, H., *Wis. Agr. Expt. Sta., Bull. 435*, 68 (1936); *Chem. Abs.*, **32**, 2633 (1938).

[25] N. V. Philips Gloeilampenfabriken, British P. 343,528, Sept. 14, 1929; French P. 700,312; *Chem. Abs.*, **25**, 3776 (1931).

[26] Campsie, H. G., U. S. P. 1,980,971, Nov. 13, 1934; *Chem. Abs.*, **29**, 498 (1935).

[27] Chaney, N. K., U. S. P. 1,842,313, Jan. 19, 1932 (to National Carbon Co.).

[28] Chaney, N. K., U. S. P. 1,894,158; *Chem. Abs.*, **27**, 2504 (1933).

[29] Geffcken, H. H., and Richter, H., German P. 523,257, Feb. 8, 1927; 526,141, May 17, 1929; Goodall, F. E., and van Sant, R. H., U. S. P., 1,735,610, Nov. 12, 1930; N. V. Philips Gloeilampenfabriken, British P. 313,558, June 14, 1928; *Chem. Abs.*, **24**, 1036 (1930); Hickman, J. O., British P. 392,626, Feb. 17, 1932; Tixier, G., British P. 376,996, July 21, 1932; Ross, J. C., U. S. P. 1,896,379; Zecher, G., U. S. P. 1,929,910, Oct. 10, 1933; *Brit. Chem. Abs.* **B**, 587 (1934); Mailey, R. D., U. S. P. 1,969,655, Aug. 7, 1934; Ban, N., van Recsey, N., and van Recsey, E., British P. 382,349, Oct. 27, 1932; Brown, G., British P. 294,502, July 22, 1927; *Chem. Abs.*, **23**, 1967 (1929); Stephens, H. C., and Hoar, S. B., U. S. P. 2,020,250; Salmony-Karsten, A., *Allgem. Oel-und Fett-Z.*, **32**, 358 (1935); Beardslee, F. C., U. S. P. 1,682,318; Linder, J., Austrian P. 125,772, July 15, 1931; Soc. anon. des usines Rémy, Belgian P. 386,419, March 31, 1932; *Chem. Abs.*, **27**, 1416 (1933).

[30] Shumway, E. D., U. S. P. 1,928,397 (to Quaker Oats Co.); *Chem. Abs.*, **27**, 5840 (1933).

[31] Dorcas, M. J., *Food Industries*, **1**, 504 (1929); *Chem. Abs.*, **32**, 4508 (1929).

[32] Jaeger, C., British P. 290,195, April 18, 1928; *Chem. Abs.*, **23**, 916 (1929).

[33] Berndt, E. C., and Creighton, H. M., U. S. P. 2,072,416-7-8 (to R. U. V. Engineering Corporation); *Chem. Abs.*, **31**, 773, 2701 (1937).

A process for making biscuits, cakes, etc. in the presence of ultraviolet light was described by Elias,[34] and an apparatus for irradiating bread was described by Kielwein.[35] McGroarty[36] proposes the irradiation of an emulsified mixture prepared from salt, sugar, milk, shortening and yeast. This is then to be mixed with an irradiated yeast suspension, flour and water, for preparing bread dough. Antirachitic biscuits, prepared either from a dough with an added vitamin D concentrate or by the irradiation of the biscuits, retain their potency even after baking at 180-200°C. according to Markar'yan.[37] Tisdall[38] prepares biscuits, cakes, rusks or breads containing vitamins A, B, E and D from bone meal, baking powder and irradiated wheat germ, whole wheat and yeast.

Detailed studies of the antirachitic potency imparted to soda crackers by exposures at 12 inches, from a mercury arc emitting 94 ergs per second per sq. mm. have been reported by Read and Bailey.[39] Activation was attained in ten seconds, according to the results of bone-ash data on animals which had been on diets containing the crackers at a 20 per cent level. In the preparation of the crackers, lard, which may contain an appreciable amount of vitamin D, was replaced by hydrogenated shortening or lards shown to lack the vitamin. It was also shown that crackers made with irradiated shortening carried their antirachitic potency through the fermentation and baking processes.

Greaves and Nielson[40] find that the addition of 0.5 gm. of irradiated Utah-grown wheat causes a slight healing in rachitic rats. This becomes pronounced with 0.75 gm. or with 1.25 gms of the unirradiated wheat. The highest provitamin content was found in the Baart and the lowest in the Kharkov varieties. Becker[41] studied the amounts of the vitamin which could be produced per hour in wheat, rye, barley, corn, peanut, linseed, sunflower-seed and pumpkin-seed meals. With the feed stationary, and exposures of 10 to 120 seconds, 160 to 1360 units were produced and in feed moving beneath the lamp in a thin layer, 1500 to 18,000 I.U. A reasonable speed is that allowing an activation of about 0.5 I.U. per gram.

The addition of 10 per cent of irradiated farina in the diet of the rat failed to cause healing of rickets in experiments by Schlutz and Ziegler.[42] Pincussen[43] believes that irradiated oats stimulate carbohydrate metabolism in rabbits. The administration of irradiated cereals to school children produced no increase in calcium and phosphorus retention beyond the limits of normal variation, according to Porter-Levin.[44] Drake and Tisdall[45] found that irradiated farina given to children on a low calcium diet caused an increased efficiency in the utilization of these elements. Autoclaving an irradiated ration for six hours at fifteen lbs. does not affect its antirachitic properties.[46]

Ultraviolet rays impart antirachitic value to lettuce, alfalfa, spinach and soybeans, but not to cabbage.[47] Greater antirachitic properties are imparted to the cut than to the intact plant, but the exposures necessary to produce the vitamin in the plant are longer than those required to produce enough to protect a directly irradiated animal.

The irradiation of three kinds of mushrooms, as well as of the autoclaved, dried and ground pad resulting from the growth of certain molds in an inorganic medium containing 4 per cent of glucose, produces the vitamin, according to Preuss, Peterson, Steenbock and Fred.[48]

[34] Elias, O. A., British P. 266,101, Jan. 12, 1926.

[35] Kielwein, F., German P. 564,401, Nov. 1, 1927; 608,277, Jan. 19, 1935; *Chem. Abs.*, **29**, 2618 (1935); German P. 647,522, July 6, 1937; *Chem. Abs.*, **31**, 8739 (1937).

[36] McGroarty, W. J., U. S. P. 1,863,277; *Chem. Abs.*, **26**, 4111 (1932).

[37] Markar'yan, E. A., *Proc. Sci. Inst. Vitamin Research, U.S.S.R.*, **1**, 198 (1936); *Chem. Abs.*, **31**, 1854 (1937).

[38] Tisdall, F. F., British P. 357,223, Jan. 24, 1930; *Chem. Abs.*, **27**, 350 (1933).

[39] Read, J. W., and Bailey, C. H., *Cereal Chemistry*, **10**, 99 (1933); *Chem. Abs.*, **27**, 2982 (1933); Wörner, A., [U. S. P. 1,796,134; *Chem. Abs.*, **25**, 2493 (1931)] claims to avoid impairment of the taste of bread by using a reflector and permitting no direct rays to strike the bread.

[40] Greaves, J. E., and Nielson, H., *Food Research*, **1**, 495 (1936); *Chem. Abs.*, **31**, 2647 (1937).

[41] Becker, J., *Mezogazdasági Kutatások*, **9**, 191 (1936); *Chem. Abs.*, **30**, 7701 (1936).

[42] Schlutz, F. W., and Ziegler, M. R., *J. Am. Med. Assoc.*, **93**, 1466 (1929); for further experiments on irradiated cereals, see Steenbock, H., Black, A., and Thomas, B. H., *J. Biol. Chem.*, **85**, 585 (1930).

[43] Pincussen, L., *Strahlentherapie*, **51**, 685 (1934); *Chem. Abs.*, **29**, 4051 (1935).

[44] Porter-Levin, T., *J. Am. Diet. Assoc.*, **8**, 482 (1933); *Chem. Abs.*, **27**, 2986 (1933).

[45] Drake, T., and Tisdall, F. F., *Canadian Med. Assoc. J.*, **26**, 296 (1932); *Chem. Abs.*, **27**, 4278 (1933).

[46] Daniels, A. L., and Jordan, D. P., *Proc. Soc. Exptl. Biol. Med.*, **26**, 453 (1929).

[47] Lojkin, M., *Contributions Boyce Thompson Inst.*, **3**, 245 (1931); *Chem. Abs.*, **25**, 5450 (1931).

June butter fat is a poor source of vitamin D but is readily activatable, a ten-minute exposure at a depth of 1.6 mm. being best.[49] It would also be possible to improve its quality by the introduction of irradiated ergosterol. Lampitt, Sylvester and Bilham[50] have described a method for the irradiation of fats in which the light reaching the cell containing the fat is standardized by the use of a simultaneously exposed calibrated photoelectric cell. This arrangement, although employed for the study of oxidation processes, would also be applicable to the formation of the vitamin.

Nomura[51] proposed to ferment mixtures of flour, fruit juices, Japanese yams, and meat or fish soup, and then irradiate, dry and powder the product.

Favorable results with irradiated chocolates were reported by Krasso.[52] McKinlay[53] exposed chocolate candy on an endless belt to a mercury arc. Ried[54] ascribed beneficial effects to the irradiation of added metals or compounds such as zinc oxide, ferrous carbonate or calcium carbonate mixed with the fatty materials in the chocolate.

Labbé[55] extracted sterols from cacao beans, separated the α- and β- sterols by crystallization, mixed and irradiated them.[56]

Drummond,[57] in discussing the public health aspects of the vitamin D fortification of foodstuffs, concludes that their promiscuous irradiation is of questionable value. He did, however, consider the addition of calciferol to milk to be justified. Another discussion involving the status of the problem of vitamin addition to foods in general use has been given by Sherman and others.[58] The possibilities of the production of vitamin D have been extended by extravagant claims. Thus, it has been proposed to impregnate textiles with materials which, upon irradiation, acquire therapeutic properties.[59]

Pharmaceutical Developments. The value of pharmaceutical preparations of D_2, Viosterol, is firmly established, and, since its use is less apt to be promiscuous, is less subject to criticism than is the general irradiation of foodstuffs. At first it was believed that the antirachitic or growth-promoting properties of cod-liver oil could be enhanced by irradiation,[60] but, as stated in the preceding chapter it is now generally recognized that the oil contains little, if any, provitamin and the effects of irradiation can only be to destroy the vitamins A and D_3 naturally present.[61] However, Coster and Günther[62] maintained that the antirachitic potency once destroyed in the hardening of cod-liver oil may be restored by irradiation.

[48] Preuss, L. M., Peterson, W. H., Steenbock, H., and Fred, E. B., *J. Biol. Chem.*, **90**, 369 (1931).

[49] Steenbock, H., Wirick, A. M., and Riising, B. M., *J. Dairy Sci.*, **13**, 497 (1930); *Chem. Abs.*, **25**, 729 (1931).

[50] Lampitt, L. H., Sylvester, N. D., and Bilham, P., *Biochem. J.*, **29**, 1167 (1935).

[51] Nomura, R., French P. 701,808, Sept. 9, 1930; *Chem. Abs.*, **25**, 4068 (1931).

[52] Krasso, H., *Wiener Klin. Wochschr.*, **42**, 898 (1929); *Chem. Abs.*, **23**, 5238 (1929).

[53] McKinlay, D., British P. 276,860, Oct. 27, 1926; *Brit. Chem. Abs.*, **B**, 858 (1927); see also Oppenheim, E., British P. 309,601, April 13, 1928; Swiss P. 142,862, April 9, 1929; French P. 672,318, March 29, 1929; *Chem. Abs.*, **24**, 2213 (1930).

[54] Ried, O., British P. 316,264, July 26, 1928; *Chem. Abs.*, **24**, 1683 (1930); *Wiener Klin. Wochschr.*, **42**, 896 (1929); *Chem. Abs.*, **23**, 5218 (1929); Austrian P. 126,148, Aug. 15, 1931; 123,648, Dec. 15, 1929.

[55] Labbé, H., French P. 700,036, Nov. 16, 1929; *Chem. Abs.*, **25**, 3409 (1931).

[56] See also for chocolate irradiation, the patents of the van Houten Co., British P. 340,580, Nov. 24, 1928; French P. 68,093.

[57] Drummond, J. C., *Chemistry and Industry*, 744 (1935).

[58] *Am. Public Health Assoc. Yearbook*, 78 (1933-4). For the engineering aspects, Gunderson, F. L., *Cereal Chem.*, **7**, 449 (1930); *Chem. Abs.*, **25**, 131 (1931). Krauss, E., and Bethke, R. M., [*Ohio Agr. Expt. Sta., Bimonthly Bull.*, **184**, 3 (1937); *Chem. Abs.*, **31**, 5886 (1937)] believe the addition of the vitamin to foods should be limited to milk. See also Fleisch, A., *Presse méd.*, **45**, 1542 (1937); *Chem. Abs.*, **32**, 3797 (1938); Knapp, A. W., *Chemistry and Industry*, 558 (1938)

[59] Lederer, B., French P. 796,046, March 27, 1936; *Chem. Abs.*, **30**, 5727 (1936).

[60] Price, W. A., *Am. J. Diseases of Children*, **33**, 78 (1927).

[61] Van Leersum, E. C., *Nederland. Tijdschr. Geneesk.*, **74, I**, 899 (1930); *Chem. Abs.* **24**, 3264 (1930).

[62] Coster, J. H., and Günther, G., Austrian P. 124,892, May 15, 1931; *Chem. Abs.*, **26**, 761 (1932).

In England, the production of ergosterol on a large scale was begun about 1928 by the British Drug Houses, Ltd. and by the Boots Drug Co., Ltd.[63] When irradiated, it was employed in margarine manufacture and in pharmaceutical preparations, such as Radiomalt, a palatable preparation which also contained vitamins A and B, and Vitamalt.[64]

Many of the patents cited in previous paragraphs apply also to the irradiation of ergosterol, but many more are concerned with this alone. Indeed, most of the developments discussed in the preceding chapter were patented. In the earlier period there were several claims which have since turned out to have little significance, or to be erroneous. The use of x-rays, cathode rays or corona discharges[65] apparently has not yet been widely applied. Claims have been made that the formation of the vitamin could be effected without the use of ultraviolet rays by treating ergosterol with metallic catalysts, such as copper, bronze and nickel.[66]

It is not possible to discuss the structural details of apparatus utilized for irradiation. At one time it was stated that the irradiated solutions should be at temperatures above 70°C.[67] Bills[68] gave details of a method for repeatedly circulating the solution through a chamber between the quartz mercury burner and the lamp casing. Fraps[69] described methods used in exposing ergosterol to sunlight.[70]

Trufanov[71] agitates the solution of ergosterol in a water-cooled quartz vessel by a flow of carbon dioxide sucked through by a vacuum pump. He alters about 50 per cent of a 2 per cent solution of the sterol in benzene, using as a source a carbon arc at a distance of 5 cm., the electrodes being composed of 65 parts carbon, 2.5 iron and 32.5 magnesia.

From and others claim[72] that infrared rays assist the formation of the vitamin by antibacterial rays from a glow discharge. They also provide means for circulating ozone. In addition, the use of dyes as sensitizers[73] has been proposed, although these substances have been said to lead to the formation of substances different from the vitamin by Windaus (chapter 39).

Apparently, the earliest commercial irradiated ergosterol product was the toxic Vigantol (chapter 39), prepared by the aid of a photoelectric device which cut off the light when the maximum absorption of wave-lengths between 2400 and 2500A had been attained.[74]

[63] Langton, H. M., *J. Soc. Chem. Ind.*, **48**, 31 (1929).

[64] Reviews of recent applications: Tabern, D. L., *Clin. Med. Surg.*, **40**, 9 (1933); Weidlich, G., *Z. Vitaminforsch.*, **2**, 253 (1933); Tanret, G., *Bull. soc. chim. biol.*, **15**, 1346 (1933); Routh, I. B., *J. Chem. Educ.*, **10**, 13 (1933); Borgeaud, P., *Bull. Soc. Vaud. Sci. Nat.*, **58**, **17**, 232 (1933).

[65] I. G. Farbenindustrie, British P. 318,269, April 2, 1928; *Brit. Chem. Abs.* **B**, 711 (1929); Whittier, C. C., U. S. P. 2,106,779, 2,106,780-1-2, Feb. 1, 1938; *Chem. Abs.*, **32**, 2692 (1938); Kramer, B., Natelson, S., and Sobel, A. E., U. S. P. 2,112,242, March 29, 1938; *Chem. Abs.*, **32**, 3913 (1938); Milas, N. A., U. S. P. 2,117,100, May 10, 1938; *Chem. Abs.*, **32**, 5161 (1938). The product known as Ertron is made by the Whittier process.

[66] Heilbron, I. M., British P. 318,268, March 2, 1928; *Chem. Abs.*, **24**, 2244 (1930).

[67] I. G. Farbenindustrie, British P. 316,803, Sept. 17, 1928; *Chem. Abs.*, **24**, 1938 (1930).

[68] Bills, C. E., U. S. P. 1,808,760, June 9, 1931; *Chem. Abs.*, **25**, 4156 (1931).

[69] Fraps, R. M., U. S. P. 2,015,264-5, Aug. 24, 1935; *Chem. Abs.*, **29**, 7587 (1935).

[70] Other patents on irradiation apparatus: Buhtz, E., German P. 514,992, June 27, 1926; Cuny, L., German P, 637,716, Nov. 3, 1936; O'Brien, B., British P, 459,043 and 459,118 ,Dec. 28, 1936; *Chem. Abs.*, **31**, 4021 (1937); Pferdemenges, H., British P. 638,338, July 27, 1927; Patent Treuhand Ges. für Elektrische Glühlampen, German P. 553,016, Dec. 21, 1927; 541,991, Oct. 30, 1927; Quarzlampen. Ges., British P. 295,023, Aug. 4, 1927; Nicholls, H. J., U. S. P. 2,070,307, *Chem. Abs.*, **31**, 2054 (1937); Tixier, G., British P. 356,083, Jan. 22, 1930; Zecher, G., U. S. P. 1,929,910; Vilenkin, M., Russian P. 25,652, March 31, 1932; *Chem. Abs.*, **26**, 5231 (1932); Hickman, J. O., British P. 392,626, May 25, 1933; Salmony-Karsten, A., *Kautschuk*, **10**, 55 (1934); *Milchwirtschaft Zentr.*, **63**, 225 (1934); *Chem. Abs.*, **29**, 236 (1935); Robinson, F. W., and Larsen, C. J., U. S. P. 2,051,395, Aug. 18, 1936.

[71] Trufanov, A. V., *Khim. Farm. Prom.*, 196, 253 (1933); *Chem. Abs.*, **28**, 498, 4108 (1934).

[72] From, V. C., Rowley, C. D., and Larsky, A. W., British P. 325,824, Feb. 2, 1929.

[73] Merck, Chemische Fabrik, British P. 286,665, March 8, 1927; *Brit. Chem. Abs.*, **B**, 836 (1928); *Chem. Abs.*, **23**, 483 (1929).

[74] British P. 296,093, Aug. 22, 1928, to I. G. Farbenindustrie A.-G.; *Brit. Chem. Abs.*, **B**, 73 (1929).

Some have attempted to prevent losses during the irradiation by the use of certain additions to the solvent. Thus, ethylene or an alkali hydroxide has been added to ether or alcohol for this purpose.[75] Brauchli[76] uses hydroquinone or other dihydroxyphenols. To obtain stable solutions, Hooper[77] dissolves the highly active transformation product of ergosterol in 1,2—,2,3—,1,3—or 1,4-butanediol or 2-methyl-1, 3-propanediol. A method has been described for extracting the reaction product from the solvent after its exit from the reaction chamber, followed by the introduction of fresh provitamin into the solvent in the reaction chamber so that the solvent may be used repeatedly.[78] The acid esters of sterols may be irradiated before they are converted into salts.[79]

Various methods have been proposed for separating the irradiation product. In one,[80] the unchanged ergosterol is separated by virtue of its small solubility in alcohol, acetone, etc. The separation is continued until the ergosterol shows a dextrorotatory power greater than 25° for the yellow line of mercury. The active material is obtained by distillation of the solvent. Light and Frey[81] carry out the irradiation in solvents such as diethylene dioxide, triethanolamine, ethyl acetate, etc., which have a much higher solvent power for the activated product than for the original ergosterol. Jendrassik[82] irradiated solid ergosterol in contact with a solution containing vitamin D or ergosterol. The solution formed was led away by dialysis and fresh solution continuously added.

Filters to eliminate various wave-lengths have been suggested. Some would remove, by a carbon disulfide filter, wave-lengths longer than 3000A, particularly the 3126 and 3132A lines of mercury, believing these to be harmful.[83]

The work of Reerink and van Wijk, discussed in the preceding chapter, has also been made the basis of patents assigned to the Philips Lamp Works.[84] This, it may be recalled, eliminates wave-lengths shorter than 2700 and longer than 3000A.

Spectrographic control of the irradiation process is specified by Zimmermann and Frankenburger[85] much as in the earlier Vigantol patents, except that it is stated that the irradiation is to be interrupted before the maximal absorption between 2300 and 3000A has been exceeded.

[75] I. G. Farbenindustrie A.-G., British P. 321,992, Oct. 25, 1928; *Chem. Abs.*, **24**, 2837 (1930); British P. 316,803, Sept. 17, 1928; *Brit. Chem. Abs.*, **B**, 836 (1929); *Chem. Abs.*, **24**, 1938 (1930).

[76] Brauchli, E., U. S. P. 1,824,653, Sept. 22, 1931 (to Hoffman LaRoche, Inc.); *Chem. Abs.*, **26**, 181 (1932); British P. 334,002, July 1, 1929.

[77] Hooper, C. W., U. S. P. 2,030,792 (Winthrop Chemical Co.); British P. 436,713, Oct. 16, 1935; *Chem. Abs.*, **30**, 1949, 2326 (1936).

[78] I. G. Farbenindustrie A.-G., British P. 314,267, Aug. 20, 1928; Frankenburger, W., and Weizel, W., German P. 491,222, May 20, 1928; *Chem. Abs.*, **24**, 2056 (1930); French P. 675,558, May 10, 1929; *Chem. Abs.*, **24**, 2674 (1930); see also Merck, German P. 556,716, March 6, 1928, for a description of an aqueous, colloidal solution of irradiated ergosterol.

[79] Hoffman-La Roche Co., German P. 567,333, Dec. 13, 1928.

[80] Soc. des usines chimiques Rhône-Poulenc, British P. 335,377, March 27, 1930; 335,277, June 25, 1929; French P. 698,040, June 11, 1930; *Chem. Abs.*, **25**, 1562, 3039 (1931).

[81] Light, R. F., and Frey, C. N., U. S. P. 1,955,554, (to Standard Brands); *Chem. Abs.*, **28**, 3752 (1934); British P. 394,408, June 29, 1933; Canadian P. 333,281, June 13, 1933; *Chem. Abs.*, **27**, 4631 (1933).

[82] Jendrassik, A., Hungarian P. 104,227, April 14, 1931; *Chem. Abs.*, **27**, 1387 (1933).

[83] N. V. Philips' Gloeilampenfabrieken, French P. 714,827, April 4, 1931; *Chem. Abs.*, **26**, 1715 (1932); French P. 737,234; May 17, 1932; *Chem. Abs.*, **27**, 1453 (1933); French P. 700,312, July 17, 1930; *Chem. Abs.*, **25**, 3776 (1931); **27**, 810 (1933); Dutch P. 32,096, Feb. 15, 1934; *Chem. Abs.*, **28**, 3842 (1934); French P. 708,548, Dec. 29, 1930; British P. 385,626, Dec. 20, 1932. Some of these deal with methods for removal of portions of the solvent and for the addition of added amounts of ergosterol.

[84] Reerink, E. H., and van Wijk, A., U. S. P. 1,904,751, April 18, 1933, to N.-V. Philips' Gloeilampenfabrieken; *Chem. Abs.*, **27**, 3560 (1933); German P. 634,146, Aug. 18, 1936; *Chem. Abs.*, **30**, 8533 (1936).

[85] Zimmermann, W., and Frankenburger, W., U. S. P. 1,896,191 (Winthrop Chemical Co.); *Chem. Abs.*, **27**, 2534 (1933).

Much of the work of the Göttingen laboratories has been patented, the United States patents being held by the Winthrop Chemical Co. Windaus [86] described the preparation of D_2 by irradiating ergosterol with light excluding wave-lengths shorter than 2750A. About 40-50 per cent conversion was obtained. Unchanged ergosterol was removed and the product was treated with citraconic anhydride for ten days in ether solution. Removal of the solvent was effected by evaporation at a low temperature. The residue is then saponified with alcoholic potassium hydroxide, diluted with water after about 12 hours, extracted with ether, petroleum ether or both, washed with water and dried. Following the latter operation, the solvent is evaporated and the residue crystallized from alcohol. Linsert [87] uses the unfiltered light of a magnesium spark, the remaining treatment being very similar to that described by Windaus. In the earlier patents, he specified the use of maleic anhydride, which left the antirachitic products in solution. Subsequently, Linsert [88] described the removal of the D_2 by the use of *m*-dinitrobenzoyl chloride in the presence of pyridine.

There are a great number of patents dealing with the introduction of irradiated ergosterol into food products. Ernotte [89] states that an aqueous-oil emulsion of vitamin D may be made with lecithin as the emulsifier.

The recent attention to a cholesterol derivative as the true provitamin of the natural antirachitic vitamin has been reflected in a patent by Waddell,[90] who described methods of treating cholesterol by mild oxidation with hydrogen peroxide or benzoyl peroxide, or by heat treatment, in order to increase the provitamin content.

The sterols of duck eggs may be irradiated to obtain preparations of antirachitic value for chickens.[91] Fats of various invertebrates may also be irradiated for this purpose.[92]

The various irradiated ergosterol preparations are very widely used,. Besides the simple vitamin D preparations, there are a great number of products in which the irradiated ergosterol is supplemented by various other vitamins. Practically all the preparations are assayed in terms of the international standard. During the early developments there were, however, considerable variations in the potency of the products, since they were assayed against samples of cod-liver oil, the potency of which was not guaranteed.[93]

[86] Windaus, A., U. S. P. 1,873,942, Aug. 23, 1932; *Chem. Abs.*, **26,** 6072 (1932); U. S. P. 1,902,745; *Chem. Abs.*, **27,** 3294 (1933); German P. 565,900, April 3, 1931, and 583,791, Sept. 9, 1933. The last describes the conversion of ergosterol to D_2.

[87] Linsert, O., U. S. P. 1,902,785; *Chem. Abs.*, **27,** 3294 (1933); German P. 576,021 and 565,900; British P. 405,321; 370,743, April 2, 1931, to I. G. Farbenindustrie A.-G.; *Chem. Abs.*, **28,** 4842 (1934).

[88] Linsert, O., German P. 603,088, Sept. 22, 1934; *Chem. Abs.*, **29,** 552 (1935); U. S. P. 2,030,377; *Chem. Abs.*, **30,** 2326 (1936). The irradiation of 22-dihydroergosterol is also described. I. G. Farbenindustrie, A.-G., German P. 642,759, March 16, 1937; *Chem. Abs.*, **31,** 6417 (1937). U. S. P. 2,128,199, Aug. 23, 1938; *Chem. Abs.*, **32,** 8702 (1938). For 7-dehydrocholesterol, see Windaus, A., and Schenck, F., U. S. P. 2,099,550, Nov. 16, 1937; *Chem. Abs.*, **32,** 312 (1938). German P. 661,686, June 24, 1938; *Chem. Abs.*, **32,** 8706 (1938). For irradiation of oxidized cholesterol, E. I. du Pont de Nemours and Co., British P. 485,452, May 17, 1938; *Chem. Abs.*, **32,** 8081 (1938).

[89] Ernotte, M., French P. 796,101, March 30, 1936; *Chem. Abs.*, **30,** 5676 (1936).

[90] Waddell, J., U. S. P. 2,028,364; *Chem. Abs.*, **30,** 1521 (1936); U. S. P. 2,056,992; *Chem. Abs.*, **30,** 8533 (1936). Pacini, A. J., U. S. P. 1,880,977-8; *Chem. Abs.*, **27,** 567 (1933) proposed the irradiation in the presence of a sensitizer such as uranium acetate. *Cf.* the work of Windaus on the course of such reactions with dyes as sensitizers.

[91] N. V. Philips' Gloeilampenfabrieken, British P. 464,066, April 12, 1937; *Chem. Abs.*, **31,** 6417 (1937).

[92] N. V. Philips' Gloeilampenfabrieken, British P. 471,994, Sept. 15, 1937; *Chem. Abs.*, **23,** 1408 (1938); British P. 477,283, Dec. 22, 1937; *Chem. Abs.*, **32,** 3913 (1938).

[93] See Holmes, A. D., and Pigott, M. G., *J. Biol. Chem.*, **64,** 263 (1925); Barnes, D. J., Brady, M. J., and James, E. M., *Am. J. Diseases of Children*, **39,** 44 (1930); De Sanctis, A. G., and Craig, J. D., *J. Am. Med. Assoc.*, **94,** 1285 (1930). For assays of German preparations, see Heubner, W., and Frerichs, M., *Arch. exptl. Path. Pharmakol.*, **165,** 553 (1932); *Chem. Abs.*, **26,** 5127 (1932).

Methods for Increasing Vitamin D in Milk.

Although rickets is not a fatal disease, it has serious consequences. Improved methods of treatment and a better understanding of the disease have lessened the number of cases in which obvious deformities have been produced. There remain many cases in which less evident skeletal changes of the chest may be produced which predispose to respiratory diseases and faulty development of the pelvic arch, the latter sometimes increasing the difficulties of childbirth. The high incidence of the disease has led to much recent work on the development of a safe, generally applicable prophylactic to be supplied in the nutrition of all infants of a community with the object of rendering subsequent treatment of the disease unnecessary. Since direct sunlight is not in all cases available in the winter months, and artificial irradiation of all infants is too expensive to be feasible, the vitamin must be supplied in the food. The only food given infants of the most susceptible age is milk, and for this reason it has been important to study its adequacy in the prophylaxis of rickets. Unfortunately, milk is low in antirachitic potency, having only about five to ten Steenbock units per quart, whereas an average infant requires 35 to 50, the equivalent of three teaspoons of cod-liver oil, in order to prevent the occurrence of rickets. According to Thomas and Cannon,[94] butter fat may contain about one Steenbock unit in 9 grams. Intensive work in the last few years has led to the proposal of a number of methods by which the antirachitic potency of milk may be rendered adequate.[95]

These may be classified as follows:

I. Treatment of the Cow
   - A. Irradiation
   - B. Addition of vitamin D to the food as
     1. Irradiated ergosterol
     2. Irradiated yeast
     3. Irradiated molds or other products
     4. Irradiated natural provitamin
     5. Concentrates from natural sources

II. Treatment of the Milk
   - A. Addition of Vitamin D as
     1. Irradiated ergosterol
     2. Irradiated natural provitamin
     3. Concentrates from natural sources
   - B. Irradiation

Antirachitic milk has the vitamin in an essential food which also supplies the necessary calcium and phosphorus.[96]

[94] Thomas, B. H., and Cannon, C. Y., *Iowa Agr. Exp. Sta. Report*, 26 (1933); *Chem. Abs.*, **29,** 3002 (1935).

[95] General reviews are due to: Oser, B. L., *Milk Plant Monthly*, **23,** No. 10, 34 (1934); *Chem. Abs.*, **28,** 7373 (1934); Tonney, F. O., *Am. J. Public Health*, **26,** 665 (1936); Olson, T., and Wallis, G., *S. Dakota Agr. Exp. Sta., Bull. 296*, 3 (1935); *Chem. Abs.*, **30,** 5666 (1936); Andresen, O., *Arch. Kinderheilk.*, **90,** 65 (1930); *Chem. Abs.*, **26,** 501 (1932); Weckel, K. G., *Milk Plant Monthly*, **23,** No. 3, 27 (1934); *Chem. Abs.*, **28,** 3490 (1934); Roadhouse, C. L., *Proc. 19th Ann. Meeting, Western Division Am. Dairy Sci. Assoc.*, 109 (1933); Ellington, E. V., *Proc. 6th Ann. State Coll. Washington Inst. of Dairying*, 17 (1933); Batchelder, E. L., *Ibid.*, 48; *7th Inst.*, 47 (1934); Auerbacher, L. J., *Med. J. Record*, Nov. 2, 16 (1932); Bunker, J., and Harris, R. S., *New England J. Med.*, **211,** 1140 (1934); Shrader, J. H., *Arch. Phys. Therap. X-Ray, Radium*, **15,** 709 (1934); *Chem. Abs.*, **29,** 1861 (1935); Barnes, D. J., *Am. J. Diseases of Children*, **48,** 1258 (1934); Tobey, J. A., *8th Ann. Report N. Y. State Dairy and Milk Inspectors*, 107 (1934); *Chem. Abs.*, **29,** 4465 (1935); Smith, C. A., *Milk Dealer*, **23,** No. 10, 38 (1934); McCollum, E. V., *Ibid.*, **24,** No. 4, 32 (1935); Kon, S. K., *J. Dairy Research*, **7,** 192 (1936); Kramer, B., and Gittleman, I. F., *New England Med. J.*, **209,** 906 (1933); Wyman, E. T., *Ibid.*, 889.

[96] Hess, A. F., *Am. J. Public Health*, **22,** 121 (1932).

That the potency of a milk depends upon the amount of sunlight to which the cow has access has been known since the first observations of the formation of vitamin D by irradiation.[97] Monthly assays conducted over a two-year period by Bechtel and Hoppert[98] indicated variations of as much as 900 per cent in antirachitic potency of the milk fats. The values were highest in July, August and September and lowest in February. Apparently, exposure to sunlight is the factor determining the activity of the milk. Guernsey milk varied from 4.8 to 43.8 U.S.P. units per quart and Holstein milk from 3.1 to 27.7. Gabathuler[99] states that milk at Davos in the Swiss Alps is twice as rich in D as milk from the plains.

Somewhat negative indications regarding the efficacy of irradiation of the cow were reported by Steenbock,[100] who was, however, concerned with the calcium balance of the lactating cow rather than with the antirachitic potency of the milk. Gowen, Murray, Gooch and Ames[101] reported that after daily exposures of cattle for fifteen to thirty minutes to ultraviolet rays, it was possible to cure rickets in chicks by feeding their milk. Similar results were reported by Falkenheim, Vöitz, and Kirsch.[102] Hess, Weinstock and Sherman[103] found irradiation of a nursing human mother to increase the antirachitic potency of her milk.

Irradiation of cows has been said also to increase the milk production by 4.77 per cent and the butter fat by 8.73 per cent.[104] Bünger,[105] however, was unable to observe significant changes in the amount of milk, its fat content, or mineral content or vitamin content in cows confined in stalls and irradiated either on the back, udders or both back and udders. The daily doses used varied from ten minutes at 100 cm. to thirty minutes at 75 cm. The irradiation period lasted about two months.

In experiments of Mitchell, Eiman, Whipple and Stokes,[106] carbon arcs were hung so that the arc formed opposite the under side of the cow's body about midway from front to back, providing a good exposure of the udders and more tender side of the body. The arcs were about 25 inches from the animals and at this distance the total ultraviolet intensity between 2000 and 4000A was 6400 microwatts per sq. cm. or 640 ergs per sq. mm. Each cow was irradiated for fifteen minutes each day on one side only. Rat assays gave an average of 22 units per qt. (controls 5 units per qt.) This milk had similar protective power on infants to irradiated milk, and appeared also to have curative power in florid rickets, although its action was somewhat slower than that of other antirachitic agents.

Hess pointed out that this method is suitable for carefully controlled herds producing certified milk. It may also be of value in smaller communities where large-scale equipment for the irradiation of milk appears to be too expensive.

It has been shown possible to increase the vitamin D content of butter fat

[97] Luce, E. M., *Biochem. J.*, **18**, 1279 (1924); Chick, H., and Roscoe, M. H., *Ibid.*, **20**, 632 (1926).

[98] Bechtel, H. E., and Hoppert, C. A., *J. Nutrition*, **11**, 537 (1936); *Chem. Abs.*, **30**, 6044 (1936); Campion, J. E., Henry, K. M., Kon, S. K., and Macintosh, J., *Biochem. J.*, **31**, 81 (1937).

[99] Gabathuler, A., *Z. Vitaminkunde*, 1 (1931); *Chem. Abs.*, **27**, 5102 (1933).

[100] Steenbock, H., Hart, E. B., Humphrey, G. C., Elvehjem, C. A., and Scott, H. T., *J. Biol. Chem.*, **67**, 371 (1926); Hart, E. B., Steenbock, H., and Scott, H. T., *Ibid.*, **66**, 441 (1925); **73**, 59 (1927).

[101] Gowen, J. W., Murray, J. M., Gooch, M. E., and Ames, F. B., *Science*, **63**, 17 (1926).

[102] Falkenheim, C., Vöitz, W., and Kirsch, W., *Klin. Wochschr.*, **5**, 2071 (1926); *Chem. Abs.*, **21**, 761 (1927).

[103] Hess, A. F., Weinstock, M., and Sherman, E., *Proc. Soc. Exptl. Biol. Med.*, **23**, 636 (1926).

[104] Iguchi, K., and Mitamura, K., *J. Faculty Agr. Hokkaido Imp. Univ.*, **24**, Pt. 2, 39 (1928); *Chem. Abs.*, **23**, 2222 (1929).

[105] Bünger, H., *Züchtungskunde*, **5**, 424 (1930); *Chem. Abs.*, **25**, 3409 (1931).

[106] Mitchell, J. M., Eiman, J., Whipple, D. V., and Stokes, J., Jr., *Am. J. Public Health*, **22**, 1220 (1932).

by feeding the cow irradiated ergosterol.[107] The ergosterol need not, however, be isolated from the yeast before irradiation. Indeed, it has been stated that irradiated yeast is more effectively utilized.

The irradiation of dried yeast was described by Kirsch.[108] Previously, there had been patents for the treatment of various yeast extracts. Feher[109] boiled yeast with alkali, mixed it with organic solvents and separated and crystallized the upper phase. The recrystallized material was irradiated in thin layers and incorporated into cocoa butter and pressed into tablets. The Merck Co.[110] proposed to treat only the non-saponifiable constituents of the yeast fat. MacLean[111] described an activated medical product obtained by incubating yeast in solutions containing phosphate and carbohydrate and subjecting the resulting sterols and fat to ultraviolet light. Autolyzed yeast has also been activated.[112]

The direct irradiation of layers of yeast about 0.1 inch thick at about a foot from a Hanovia burner was patented by Hall.[113] Favorable reports on the irradiation of beer yeast with wave-lengths 2970 to 3020A were rendered by Schübel and Gehlen.[114] According to Coward,[115] exposure to strong sunlight suffices. The ability of irradiated yeast to protect young rats has been repeatedly demonstrated, and the material retains its potency for months or even years.[116] Kon,[117] however, noted a toxic effect to follow the prolonged administration of this material at a 1 per cent level, although Matzko[118] did not observe this in the case of the use of customary amounts of a bakers' yeast irradiated to a potency of 5,000 to 10,000 units per gram.[119]

The daily administration of 500 I.U. of the vitamin in irradiated yeast during the five winter months to 69 normally growing infants protected them from moderate or marked rickets, and definite healing could also be effected within a month in marked rickets by this dose or its double.[120]

The addition of irradiated yeast to the diet of cows was not found to alter either the assimilation of calcium and phosphorus or the quantity or quality of the milk by Hart, Steenbock, Kline and Humphrey.[121] Kieferle[122] agreed that there is no increase in the milk yield, but found an increase in its D content and a shortening of the lapse in the lactation period. The melting point of the milk fat was increased slightly and there was a slight decrease in the refractive index and in the Reichert-Meissl number. Others, however, have claimed to find an increase in the secretion of milk.[123] Kroon[124] found the increase as much as

[107] Thomas, B. H., and MacLeod, F. L., *Science*, **73**, 618 (1931). Gerstenberger, H. J., and Horesch, A. J., *J. Nutrition*, **5**, 479 (1932); *Chem. Abs.*, **26**, 5616 (1932)] found that milk from cows receiving large daily doses (200,000 rat units) was only mildly antirachitic, 9 quarts being slightly less active than a teaspoonful of cod-liver oil.

[108] Kirsch, W., *Biochem. Z.*, **196**, 294 (1928).

[109] Feher, G., Hungarian P. 100,696, Aug. 4, 1927; *Chem. Abs.*, **25**, 2524 (1931).

[110] E. Merck Co., British P. 285,083, Feb. 9, 1928; *Chem. Abs.*, **22**, 4726 (1928); *Brit. Chem. Abs.*, **B**, 264 (1929).

[111] MacLean, I. S., British P. 295,757, May 23, 1927; *Brit. Chem. Abs.*, **B**, 797 (1928).

[112] Matsuoka, H., *Trans. Tottori Agr. Sci.*, **3**, 32 (1931); *Chem. Abs.*, **26**, 1645 (1932).

[113] Hall, P., British P. 354,371, May 8, 1930; *Chem. Abs.*, **26**, 3870 (1932).

[114] Schübel, K., and Gehlen, W., *Arch. Exptl. Path. Pharmakol.*, **166**, 348 (1932); *Chem. Abs.*, **26**, 5611 (1932).

[115] Coward, K., *Lancet*, **II**, 920 (1933); *Chem. Abs.*, **28**, 509 (1934).

[116] Vadimov, V., Voznava, A., and Semashko, V., *Elektrisikatzya Sel'skogo Khozyaistva*, **2**, No. 8, 20 (1932); *Chem. Abs.*, **27**, 1032 (1933).

[117] Kon, S. K., *Lancet*, **II**, 579 (1931); *Chem. Abs.*, **27**, 3242 (1933).

[118] Matzko, S. N., *Arch. Tierernährung Tierzucht.*, **9**, 623 (1933); *Chem. Abs.*, **28**, 6177 (1934).

[119] Sveshnikova, N. P., *Trans. Dynamics of Development (U.S.S.R.)*, **9**, 311 (1935); *Chem. Abs.*, **30**, 3032-3 (1936).

[120] Drake, T., Tisdall, F. F., and Brown, A., *J. Nutrition*, **12**, 527 (1936); Drake, T., *Am. J. Diseases of Children*, **53**, 754 (1937). For Russian work on the value of various irradiated yeasts in poultry feeding, see Kratinova, E. P., and Pokhil. A. I., *Problems Animal Husbandry (U.S.S.R.)*, **1935**, No. 9, 93; *Chem. Abs.*, **30**, 2614 (1936); Zavadovskiĭ, M., Lepskiĭ, S., Kasheninnikova, A., Samokhvalova, G., and Balezin, P., *Trans. Dynamics of Development (U.S.S.R.)*, **9**, 269 (1935); *Chem. Abs.*, **30**, 3032 (1936).

[121] Hart, E. B., Steenbock, H., Kline, O. L., and Humphrey, G. C., *J. Biol. Chem.*, **86**, 145 (1930).

[122] Kieferle, *Proc. World's Dairy Congr. Copenhagen*, Sect. I, 166, 1931; *Chem. Abs.*, **27**, 755 (1933).

[123] Bilek, F., and Hynek, L., *Zemed Arch.*, **22**, 449 (1931); *Chem. Abs.*, **28**, 3447 (1934); Poelt, H., *Z. Vitaminforschung*, **1**, No. 4 (1932); *Chem. Abs.*, **28**, 1420 (1934).

[124] Kroon, H. M., *Milchwirtschaft Zentr.*, **60**, 325 (1932); *Chem. Abs.*, **26**, 3852 (1932).

25 to 30 per cent in the yield of milk as a result of feeding the yeast for three weeks after calving. Whatever may be true concerning the effect on the yield of milk, there have been many to show increases in the D potency when as much as 200 grams are fed daily.[125] Woelffer[126] found ten ounces of yeast of 30 D potency given daily to cows yielding thirty pounds of milk gave the milk a potency of 160 Steenbock units per quart. Yeast-fed cows require fifteen to twenty days to produce milk of the maximum potency, which is approximately 432 U.S.P. units per quart. High producers are more efficient than low producers in transferring the vitamin from the yeast to the milk. For efficient utilization, the yeast must be fed at least twice daily.[127]

Higher potencies can be produced by feeding irradiated yeast than irradiated ergosterol as the source of the vitamin.[128] At about 180,000 units per cow per day, the potency of the yeast-milk may reach 150 to 160 rat units per quart, whereas that after feeding an equivalent number of units of irradiated ergosterol contains only 120 to 130. At lower feeding levels, however, the two sources are comparable in their results, but only a slight increase in the potency of the milk results. When the ergosterol fed was increased to 300,000 units, less than 2 per cent of the units ingested appeared in the milk.

There is little doubt that the method is a practical one for enriching the milk, but it is not as cheap as the direct irradiation of the milk. Spickard[129] believes irradiated milk with but 50 to 60 units per liter as effective as yeast-milk with 160 units per liter.

It is also possible to feed the cow irradiated dried molds. Thomas and Cannon[130] find that this has its greatest effect during the first few days of the feeding. After this, there is a rapid decline in the amount of the D secreted. In general, they believe the cow very inefficient in transferring added vitamin D from her diet to her milk. It is, of course, also possible to add concentrates from liver oils or other natural sources to the diet of the cow.

Such concentrates are, however, more commonly added to the milk to avoid the inefficiency of the transfer.[131] Zucker[132] adds a cod-liver oil concentrate in the proportion of one part in 12,000 of milk and obtains probably 150 units per quart, equivalent to about three teaspoons of cod-liver oil. Post[133] described concentrates by which milk may be fortified to 1500 U. S. P. units per quart. Some ergosterol irradiation products have occasionally been suggested.

Yeast-milk is particularly of value on the certified farm where the ration can be thoroughly controlled.[134] It is scarcely applicable to the general supply of cities which may require thousands of farms to meet their demand. For this purpose, direct irradiation of the milk is the most suitable method. By this method

[125] Lepsky, S., *Z. Zücht. B., Tierzücht.*, **26**, 237 (1933); *Chem. Abs.*, **27**, 2987 (1933); Golf, A., and Seeling, K., *Biedermann's Zentr. B., Tierernährung*, **6**, 65 (1934); *Chem. Abs.*, **28**, 2036 (1934); Schieblich, M., *Biedermann's Zentr. B., Tierernährung*, **6**, 71 (1934); *Chem. Abs.*, **28**, 2036 (1934).

[126] Woelffer, E. A., *Cornell Veterinarian*, **23**, 313 (1933); *Chem. Abs.*, **28**, 3109 (1934); see also Smith, C. A., *Milk Plant Monthly*, **23**, No. 5, 24 (1934); *Chem. Abs.*, **28**, 4458 (1934).

[127] Krauss, W. E., and Bethke, R. M., *Ohio Agr. Exp. Sta. Bimonthly Bull.*, **173**, 52 (1935); *Chem. Abs.*, **29**, 5525 (1935).

[128] Russell, W. C., Wilcox, D. E., Waddell, J., and Wilson, L. T., *J. Dairy Sci.*, **17**, 445 (1934); *Chem. Abs.*, **28**, 5508 (1934).

[129] Spickard, V. W., *Northwest Med.*, **33**, 204 (1934); *Chem. Abs.*, **29**, 4465 (1935).

[130] Thomas, B. H., and Cannon, C. Y., *Iowa Agr. Exp. Sta. Report on Agr. Research*, 49 (1934); 26 (1933); *Chem. Abs.*, **29**, 3002, 3375 (1935).

[131] Krauss, W. E., and Bethke, R. M., *Ohio Agr. Exp. Sta. Bimonthly Bull.*, **162**, 77 (1933); *Chem. Abs.*, **27**, 4563 (1933); Krauss, W. E., Bethke, R. M., and Wilder, W., *J. Dairy Sci.*, **16**, 549 (1933); Wyman, E. T., *New England J. Med.*, **209**, 889 (1933).

[132] Zucker, T. F., *Am. J. Public Health*, **23**, 10 (1933).

[133] Post, C. I., *Milk Dealer*, **24**, No. 3, 39 (1934); *Chem. Abs.*, **29**, 4843 (1935).

[134] Hess, A. F., Lewis, J. M., MacLeod, F. L., and Thomas, B. H., *J. Am. Med. Assoc.*, **97**, 370 (1931).

the milk acquires a potency of about 135 U.S.P. units per quart. An outstanding advantage of the method is the reduction of the human element of error to a minimum by the development of irradiation equipment mechanically controlled. It is also possible that the provitamin in milk is that which on irradiation yields a product more suited to the human than that from ergosterol. Hess[135] early showed the effectiveness of irradiated dried milk in infant feeding, as well as of irradiated yeast.

Another advantage of irradiating milk is the fact that it contains but a limited quantity of the provitamin so that too high a potency cannot be attained, thus avoiding any danger of an overdose.[136] Its use also requires no coöperation on the part of the mother and eliminates the giving of cod-liver oil.

In 1925, Steenbock, Hart, Hoppert and Black[137] found it possible to increase the antirachitic potency of cow milk more than eight times by exposing it to a quartz mercury arc. That of goat milk could be increased twenty-four times. Milk irradiated on a large scale by the methods of Supplee and Dorcas has been extensively studied in the laboratory and clinic by Hess and Lewis[138] who find it a highly effective and reliable antirachitic agent. A quart or even less of the milk daily sufficed to protect infants from rickets, although this amount contained only 50 units as assayed by a standard rat method. The full explanation as to why smaller numbers of rat units are adequate when given in this form than in cod-liver oil has not yet been given. That it might be more effective than an equivalent number of rat units of irradiated ergosterol could be accounted for by a difference in the structures of the vitamins, the human differentiating between these although the rat does not. But presumably the natural vitamin in cod-liver oil is the same as that of milk so that the doses from the two sources which are equally effective on the rat should also be equally effective on the human. This assumption has, however, not yet been proved and it must remain an assumption until the vitamin has been isolated from irradiated milk and compared chemically with D_3. Other suggestions for the discrepancy may be offered. It may be related to the presence of other substances in the milk and in the cod-liver oil which alter the ease of absorption of the vitamin.[139] Supplee, Ansbacher, Bender and Flanigan[140] attribute the unexpected effectiveness of irradiated milk to the formation of a "symplex system" between the vitamin and a colloidal carrier such as lactalbumin. This they believe can form only in lipid-free lactalbumin. When lipids are present, the vitamin merely dissolves in the prosthetic group or lipid associated with the lactalbumin. This they suggest accounts also for the observation of Lewis[141] that vitamin D administered in the water phase with propylene glycol with accompanying milk constituents is more effective than when it is carried by an oil vehicle. Ansbacher and Supplee had found that about 18 per cent of the total milk cholesterol is associ-

[135] Hess, A. F., *J. Am. Med. Assoc.*, **89**, 337 (1927); see also Eddy, W. H., *Arch. Pediat.*, **44**, 320 (1927); Supplee, G. C., and Dow, O. D., *Am. J. Diseases of Children*, **34**, 364 (1927); *J. Biol. Chem.*, **75**, 227 (1927); **73**, 617 (1927).

[136] Mohr, W., Kulteren, S., and Richter, V., *Molkerei-Z., Hildesheim*, **45**, 545 (1931); *Chem. Abs.*, **26**, 3010 (1932).

[137] Steenbock, H., Hart, E. B., Hoppert, C. A., and Black, A., *J. Biol. Chem.*, **66**, 441 (1925).

[138] Hess, A. F., and Lewis, J. M., *J. Am. Med. Assoc.*, **99**, 647 (1932). An early German product—Hanauer milk—had an activity such that 100 cc. corresponded to 5-6 gram of commercial cod-liver oil. Bamberger, P., *Deut. med. Wochschr.*, **55**, 1547 (1929); *Brit. Chem. Abs.*, **B**, 637 (1930).

[139] For evidence of the disparity of doses see, Hess, A. F., Lewis, J. M., McLeod, F. L., and Thomas, B. H., *J. Am. Med. Assoc.*, **97**, 370 (1931); Wyman, E. T., and Butler, A. M., *Am. J. Diseases of Children*, **43**, 1509 (1932); Gerstenberger, H., and Horesh, A., *J. Nutrition*, **5**, 479 (1932); Hess, A. F., and Lewis, J. M., *J. Am. Med. Assoc.*, **99**, 647 (1932); **101**, 181 (1933).

[140] Supplee, G. C., Ansbacher, S., Bender, R. C., and Flanigan, G. E., *J. Biol. Chem.*, **114**, 95 (1936); Ansbacher, S., and Supplee, G. C., *J. Biol. Chem.*, **105**, 391 (1934).

[141] Lewis, J. M., *J. Pediatrics*, **6**, 362 (1935).

ated with proteins, chiefly lactalbumin. It is to this prosthetically bound, cholesterol-like lipid, rather than to that free in the butter-fat, that they attribute the ability to form, on irradiation, a particularly effective antirachitic agent.

Before describing the methods employed by Supplee and others, brief mention will be made of the difficulties which must be overcome and of some of the methods proposed in Germany and elsewhere. The early attempts to irradiate milk were usually marked by a tendency to overirradiate it with resultant deterioration in odor and taste. Schultz [142] attributed this to the action of hydrogen peroxide upon the protein and found that this change did not parallel the production of the antirachitic potency. The irradiation of the cream alone did not affect the taste. He claimed that 15 grams of irradiated protein-free milk-fat cured rickets in children.[143] As yet, however, relatively little is known as to the nature of the deterioration due to overirradiation. Energy between 2600 and 3100A appears less active in flavor production than that of wave-lengths shorter than 2600A. The range from 3100 to 3800A is more active in causing flavor changes than that from 3800 to 7000A.[144]

Anderson and Triebold [145] passed milk through a commercial irradiator eight times and could detect no marked changes in the chemical composition or in the fat constants. Although the induction period for the oxidation of the fat was reduced from twenty to seventeen hours by irradiation, the rate of deterioration over a period of six months was unchanged. Digestion studies *in vitro* with pepsin and with trypsin indicated a slightly increased rate in the early stages due possibly to the destruction of an antienzyme. Hoffman [146] used a mercury-argon discharge tube which emits little heat radiation [147] in the effort to lessen the changes in taste. To overcome the difficulty of a lack of penetration of the milk by the effective rays (not over 0.1 mm.), he arranged to have it flow through an adjustable slotted distributor onto a cylindrical net of narrow-mesh wire in the center of which was placed the source. For treating raw milk, he conducted the process in the presence of an inert gas to avoid the destructive action of ozone on vitamins A and C.

Commercial milk irradiation appears to have been first carried out in Germany. It is not feasible to give the details of the apparatus there suggested.[148]

The Dry Milk Co.[149] proposed to spray the milk (liquid or powdered) before the source for a period as short as eight seconds which, with the intensities used, permitted the development of 75 per cent of the possible antirachitic potency before the formation of a disagreeable odor or taste. Most irradiate the milk in thin flowing films.[150]

Salmony-Karsten [151] believed it necessary to use an inert gas to exclude oxygen

[142] Schultz, O., *Milchw. Forsch.*, **4**, 37 (1927); *Chem. Abs.*, **21**, 3631 (1927).

[143] Schultz, O., *Klin. Wochschr.*, **6**, 848 (1927); Schultz, O., and Rohr F., *Deut. med. Wochschr.*, **33**, 1255 (1927).

[144] Weckel, K. G., Jackson, H. C., Haman, R., and Steenbock, H., *Ind. Eng. Chem.*, **28**, 653 (1936).

[145] Anderson, A. K., and Triebold, H. O., *J. Dairy Sci.*, **15**, 469 (1932); *Chem. Abs.*, **27**, 784 (1933).

[146] Hoffman, *Proc. 8th World Dairy Conference*, 460 (1928); *Chem. Abs.*, **23**, 5491 (1929).

[147] From, V. C., Rowley, C. D., and Larsky, A. W., British P. 346,682, Oct. 15, 1929; *Chem. Abs.*, 26, 537 (1932) specify the simultaneous use of infrared rays.

[148] Geffcken, H. H., and Richter, H., German P. 557,334, March 19, 1927; 545,080, March 19, 1927; 545,886, Jan. 3, 1928; Löwenstein, L., German P. 552,263, June 6, 1928; *Chem. Abs.*, **27**, 353 (1933); Schindler, A., German P. 572,491, Feb. 8, 1927; Wiegand, K., German P. 541,991, Oct. 30, 1927; 553,016, Dec. 21, 1927; Ried, O., Austrian P. 116,463, Sept. 15, 1929; *Chem Abs.*, **24**, 2837 (1930); Kirsch, W., *Chem. Fabrik*, 150 (1928).

[149] British P. 298,585, June 11, 1927, to Dry Milk Co.; *Brit. Chem. Abs.*, **B**, 911 (1928).

[150] Trebler, H. A., U. S. P. 2,001,555; British P. 428,434, May 13, 1935. In this a single unit irradiates several flowing sheets of milk. Trebler, H. A., and Larsen, C. J., U. S. P. 2,018,332; British P. 432,011, July 18, 1935; see also Robinson, F. W., and Larsen, C. J., U. S. P. 2,051,395; Cuny, L., British P. 441,524, Jan. 21, 1936; Berndt, E. C., and Creighton, H. M., U. S. P. 2,065,054-5, *Chem. Abs.*, **31**, 773, 2701 (1937); Henszey, R. O., U. S. P. 2,060,865, *Chem. Abs.*, **31**, 1665 (1937).

[151] Salmony-Karsten, A., *Chimie et industrie*, **22**, 259 (1929); Chesney, J., U. S. P. 1,723,603, Aug. 6, 1929; *Chem. Abs.*, **23**, 4512 (1929) also excluded air.

and also to add a means for cooling the milk during the process. Hickman and Hickman [152] pointed out that exclusion of air is unnecessary when the milk is exposed while flowing in a thin film on one side of a milk cooler. The irradiation is for a period of 8 to 30 seconds at a distance of 11 inches from a 2000 c.p. quartz mercury-vapor lamp with reflectors.

Since it is a lipid that is the provitamin, the question has been raised as to whether it might not be better to irradiate the cream separately. Essig [153] found irradiated skimmed milk to be only slightly protective, although the same whole milk when irradiated was highly effective. Kersten and Schultz [154] irradiate the cream and then return it to the milk from which it had been separated. Recently, however, Supplee gave reasons for believing that the effectiveness depends in some manner upon an association of the vitamin with lactalbumin, so that the separation of the cream seems unnecessary. Furthermore, Dorcas and Supplee [155] find that under given irradiation conditions, the potencies which can be attained are not in proportion to the amount of fat present. Relatively high potencies are shown in samples with low amounts of fat. Krauss, Bethke and Washburn,[156] find, however, that as the fat percentage increases, the activatability is also increased. Still the solids-not-fat fraction of Holstein milk may contain more of the provitamin than that of Jersey milk, since the two milks can be activated to the same extent even though the Jersey milk contains more fat and has a higher original potency.

Hoefelmayr [157] described the irradiation of condensed, dried or curdled milk. Favorable results of clinical studies on the use of irradiated powdered whole milk were reported by De Sanctis, Ashton and Stringfield.[158] Weckel and Jackson [159] believed the most feasible method of irradiating milk was after evaporation of raw standardized milk at 208-210°F. until it contained 7.8 to 8.3 per cent of fat. The hot milk from the vacuum pan was then irradiated by a carbon arc by passage over a conical irradiator, after which it was homogenized, canned and sterilized. When diluted to the solid content of normal milk, the vitamin potency was 50 Steenbock units per quart, corresponding to 135 U.S.P. units. Cream could be successfully irradiated without the formation of undesirable flavors or chemical deterioration. Acids developed somewhat more slowly in irradiated than in untreated milk. Supplee, Bender, Flanigan, Dorcas and Greider [160] find, however, that the irradiation of evaporated milk does not result in as high a degree of potency as the irradiation of fluid milk when films of the same capacity* are subjected to the same intensity and quality of ultraviolet radiations. Since the films of the same capacity of evaporated milk are thicker and more dense than those of fluid milk, the penetration is correspondingly less. Greater antirachitic potency of evaporated milk may be attained by the exposure of thinner films for longer periods of time or by increasing the intensity of the source, but it still does not equal that attainable by

[152] Hickman, J. O., and Hickman, N. V., British P. 325,470, Sept. 12, 1928; *Brit. Chem. Abs.*, **B**, 484 (1930). See also Bragg, J. H., U. S. P. 1,954,065, April 10, 1934; *Chem. Abs.*, **28**, 3807 (1934).

[153] Essig, B., *Münch. med. Wochschr.*, **78**, 273 (1931); *Chem. Abs.*, **25**, 4924 (1931).

[154] Kersten, G., and Schultz, O., German P. 577,531, June 1, 1933; *Chem. Abs.*, **28**, 541 (1934).

[155] Dorcas, M. J., and Supplee, G. C., *J. Dairy Sci.*, **17**, 433 (1934).

[156] Krauss, W. E., Bethke, R. M., and Washburn, R. G., *J. Dairy Sci.*, **19**, 739 (1936).

[157] Hoefelmayr, K., British P. 265,910, Feb. 12, 1926; *Chem. Abs.*, **22**, 468 (1928).

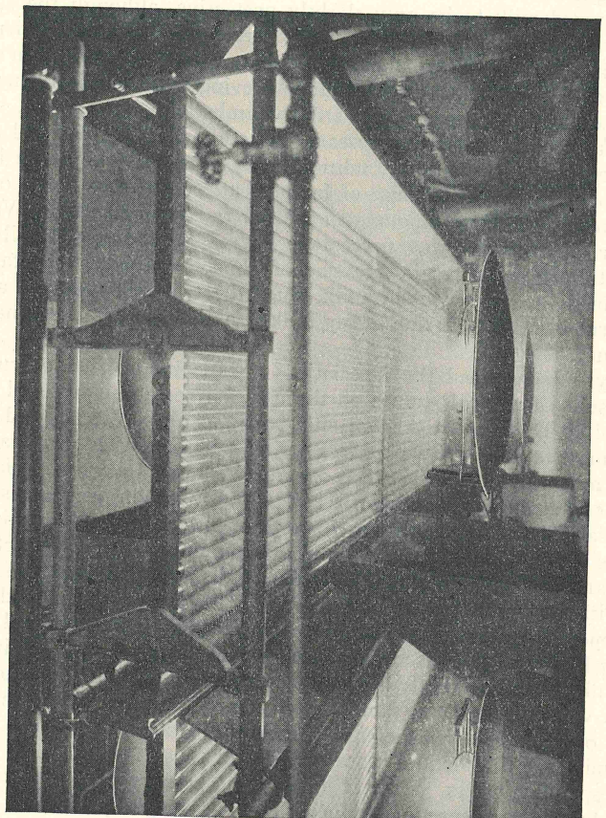
[158] De Sanctis, A. G., Ashton, L. O., and Stringfield, O. L., *Arch. Pediat.*, **46**, 297 (1929); *Chem. Abs.*, **23**, 3956 (1929).

[159] Weckel, K. G., and Jackson, H. C., *Natl. Butter and Cheese J.*, **25**, No. 11, 24 (1934); *Chem. Abs.*, **28**, 5857 (1934); *Wisconsin Agr. Exp. Sta., Bull. 428*, 33 (1934); *Chem. Abs.*, **29**, 3052 (1935).

[160] Supplee, G. C., Bender, R. C., Flanigan, G. E., Dorcas, M. J., and Greider, C. E., *J. Dairy Sci.*, **19**, 67 (1936).

* The capacity is the film thickness times the distance of film travel.

the irradiation of fluid milk films. The degree of activation imparted to evaporated milk is not significantly different when homogenized and non-homogenized products are irradiated nor is it affected by varying the temperature between 55 and 165°F. The ultraviolet transmission is progressively decreased by preheating to 180°F., by concentration and by homogenization, as a result of physical changes in the inherent milk constituents.



Courtesy National Carbon Co., Inc.

FIGURE 156. Flat Type Milk Irradiating Unit.

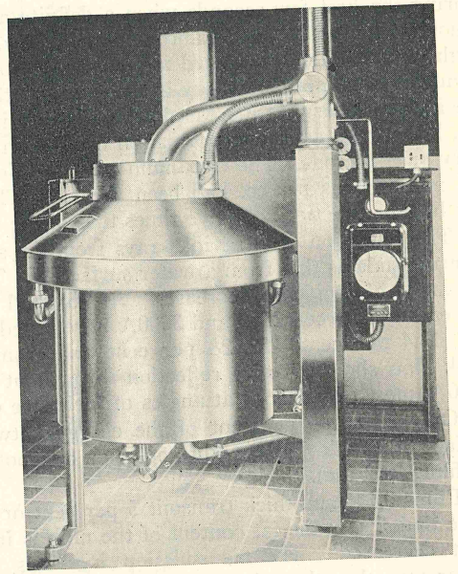
From an engineering point of view the process has been studied most thoroughly by Supplee and co-workers. The most significant feature which has emerged under commercial conditions (treatment of 1000 lb. lots) is that the time of irradiation by either a quartz mercury-vapor lamp or a carbon arc need be but a few seconds, obviating changes in taste.[161]

The milk in 1000 lb. lots was exposed as a moving film (0.4 mm.) which received the rays at constantly changing angles of incidence varying from 0 to 90°. The

[161] Supplee, G. C., and Dorcas, M. J., *Lait*, **14**, 1, 125 (1934); *Chem. Abs.*, **28**, 3143 (1934); Supplee, G. C., U. S. P. 1,817,936, Aug. 11, 1931 (to Borden Co.); *Chem. Abs.*, **25**, 5477 (1931); Supplee, G. C., Dorcas, M. J., and Hess, A. F., *J. Biol. Chem.*, **94**, 749 (1932)

complete cycle of exposure to the range of impingement angles required a period of about 0.3 second. The maximum potency was found to be attained within the first few seconds. Over 238 variations in the irradiation conditions were studied in this investigation.

There are two main types of apparatus which are employed in conjunction with the carbon arc, the flat and drum types (Figures 156 and 157). Units of various capacities have been employed. The capacity may be as low as 625 quarts per hour, and from these larger synchronized units may be assembled. A unit employed early by the Dryco Co.[162] had a normal capacity for the treatment of more than 5000 quarts per hour.



Courtesy National Carbon Co., Inc.

FIGURE 157.

National Type YN Milk Irradiating Unit.

Supplee, Beck and Dorcas,[163] by comparing the quanta of energy applied per cc. with the molecules of vitamin D formed per cc. showed that the potency is dependent upon the amount of energy applied, provided that the radiations lie within the antirachitic range. It was immaterial whether the energy was from the Corex D filtered or unfiltered carbon arc or consisted of reflected rays only. This was true within the limits of energy of 409×10^3 ergs (545×10^{14} quanta) and 9486×10^3 ergs ($12{,}480\times10^{14}$ quanta). Mica screens which transmit practically no energy below 2900A and only 45 per cent at 3150A do not permit any source to increase the potency of the milk. The relative effectiveness of an equivalent amount of energy from different sources was in the following order: C carbon, Mg carbon, mercury arc and Sunshine carbon. When time and intensity were taken into account for practical purposes the effectiveness of the sources tested increased in the order: Mercury-vapor arc, Sunshine carbon arc, magnesium carbon arc and

[162] Mitchell, J. M., Eiman, J., Whipple, D. V., and Stokes, J., Jr., *Am. J. Public Health*, **22**, 1220 (1932).

[163] Supplee, G. C., Beck, H. H., and Dorcas, M. J., *J. Biol. Chem.*, **98**, 769 (1932).

C carbon arc. The use of Corex D filters reduces the amount of energy reaching the milk per unit of time and causes a commensurate reduction in the rate of building up the potency. The effects of chromium-plated reflectors on the energy incident at normal incidence on milk at 61 cm. from an arc have been computed by Supplee, Hanford, Dorcas and Beck,[164] for the wave-length ranges 2,000-2,200A, 2,200-2,400A and 2,400-3,000A.

It was found by biological assays that the total quanta which must be applied to produce a plus-one line test in the rachitic rat was 5949×10^{15}. From the quantity of irradiated milk required and the assumptions that this must be equivalent to 0.03γ of D_2 and that its molecular weight is that of ergosterol, it was concluded that there had been produced 4.5×10^{13} molecules of the vitamin. (This implies that during the first few seconds when a definite amount of energy produces a definite amount of vitamin, the quantum yield is low, about 7×10^{-6}. Compare with the high quantum yields reported for the irradiation of ergosterol solutions, chapter 39. Evidently much of the energy is absorbed by other constituents of the milk). When the incident energy is increased beyond a certain point, $2{,}000\text{-}3{,}000 \times 10^{14}$ quanta per cc., little or no additional formation of vitamin occurs or destruction begins within very brief periods. The maximum concentration was reached after a total of about 2.5 million ergs per cc. had been applied. The concentration is then about 2.5γ per liter or practically twelve times that of the untreated milk.

The reflection of ultraviolet rays from the surface of milk is of the same order of magnitude as that from a water surface.[165] The degree of reflection increases as the angle of incidence decreases. At 75° and 45° incidence, about 3 per cent of the energy between 2550 and 3000A is reflected. At 30°, it is about 6 per cent, at 20° 13.4 per cent, 15° 28 per cent and from a 10° angle about 34 per cent. Milk films show selective reflection throughout the range of wave-lengths 2550 to 3300A, most pronounced at angles of incidence of 30° or less.

Only 20 to 40 per cent of the energy between 2500 and 2850A striking the surface of a milk film at right angles on a smooth quartz flowboard are transmitted by films 0.02 mm. thick.[166]

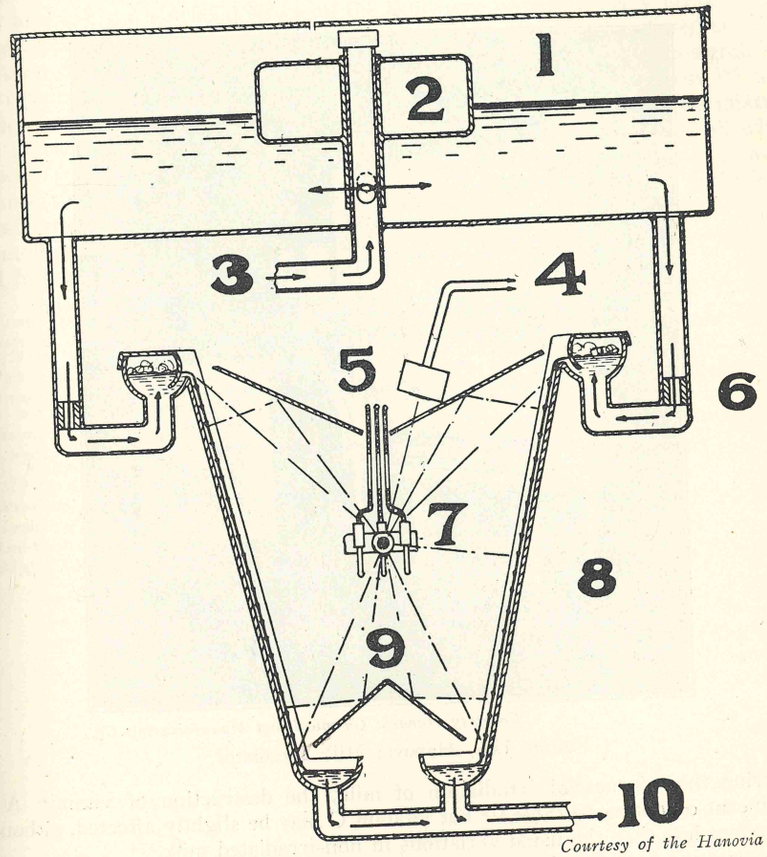
Films 0.11 mm. thick transmit 5 per cent or less of the incident energy within these limits. As the fat content of the milk is increased, the transmission is somewhat decreased. The transmission increases rapidly and progressively in the longer wave length region 2800 to 3300A.

Under suitable conditions of high intensity, a high degree of activation can be obtained from exposures varying from less than a second to not more than two seconds. It is probable that the reaction occurs chiefly at the moving surface since extremely thin but slow-moving films showed a lower degree of activation after momentary exposure than did thicker but faster-moving ones. With high intensities it is also possible to produce measurable antirachitic properties in milk derivatives containing little or no butter fat.[167] Studies on the influence of various changes in film capacity, (that is film thickness × the distance of film travel), have also been reported.[168]

Whole milk irradiation units are made by the Cherry-Burrell Corporation, the Creamery Package Manufacturing Co.[169] and the Hanovia Co. (Figures 158 and 159).

[164] Supplee, G. C., Hanford, Z. M., Dorcas, M. J., and Beck, H. H., *J. Biol. Chem.*, **95**, 687 (1932).
[165] Supplee, G. C., and Dorcas, M. J., *J. Dairy Sci.*, **17**, 607 (1934).
[166] Dorcas, M. J., and Supplee, G. C., *J. Dairy Sci.*, **17**, 433 (1934).
[167] Supplee, G. C., Flanigan, G. E., Bender, R. C., and Dorcas, M. J., *J. Dairy Sci.*, **17**, 483 (1934).
[168] Supplee, G. C., and Dorcas, M. J., *J. Dairy Sci.*, **17**, 527 (1934).
[169] British P. 450,341, July 15, 1936, to Creamery Package Manufacturing Co.

In these,[170] the milk is exposed while flowing on nearly vertical metal surfaces in thin films of about 300 to 350 lbs. per horizontal linear foot per hour. The effective distances traversed during exposure range from 9 to 60 inches in different types of equipment, using various sources and operating intensities. By means of a reflected light beam method, Beck and Weckel[171] determined the thickness at various horizontal levels of milk flowing by gravity in films of various capacities (lbs. per linear foot per hour) over vertical steel surfaces. At 200 lbs. per foot per hour or less, the films



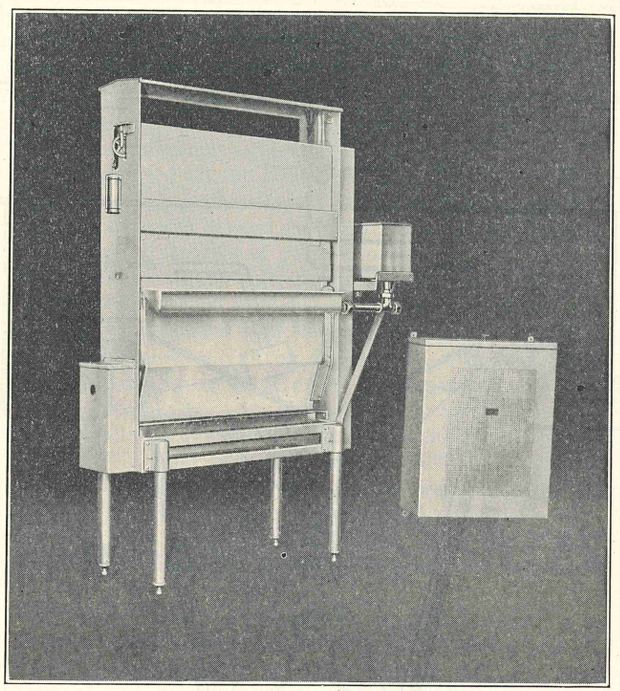
Courtesy of the Hanovia Co.

FIGURE 158. Diagram of Hanovia Milk Irradiator.

are of uniform thickness throughout their course of flow. At 300 lbs. per foot per hour, the thickness is variably greater in the first two or three inches of travel, but then becomes uniform. Under these conditions, the motion is accelerated at a decreasing rate in the first two or three inches, after which the flow attains a steady rate. For practical purposes, the average time for films of various capacities to traverse given distances is directly proportional to the distance traversed. A direct proportion between travel time and D potency was established. This may be due to the fact that the flow is turbulent, causing an interchange of substances in the surface zone within which

[170] Beck, H. H., and Weckel, K. G., *Ind. Eng. Chem.*, **28**, 1251 (1936).
[171] Beck, H. H., and Weckel, K. G., *Ind. Eng. Chem. (Anal. Ed.)*, **8**, 258 (1936). See also Beck, H. H., Jackson, H. C., and Weckel, K. G., *Ind. Eng. Chem.*, **30**, 632 (1938).

the absorption and reaction occurs. The thickness of the film in thousandths of an inch may be calculated from the capacity X by the expression: $T=1.79\ X^{0.375}$. The average velocity in inches per second is given by $0.349\ X^{0.625}$. The potency has a parabolic relation to the amount of active radiation applied, and the film capacity-potency relation is hyperbolic. O'Brien, McEwen and Morgareidge[172] calculate that if all the provitamin in whole milk could be converted, the potency would be 2.0 I.U. per gram. Using arc inputs of 300 joules per gram, they obtained 1.65 I.U. per gram.



Courtesy Hanovia Chemical and Manufacturing Co.

FIGURE 159. Hanovia Milk Irradiator.

During the commercial irradiation of milk, the destruction of vitamin A is insignificant or not measurable,[173] but vitamin C may be slightly affected, although to an extent less than the usual variations in non-irradiated milk.[174]

The question has often been raised as to whether better prophylactic results can be obtained by irradiation than by the administration of the vitamin in some form. Apparently, there is little if any difference, but since radiation therapy is less readily available the latter must usually be relied upon in practice.[175]

[172] O'Brien, B., McEwen, H. D., and Morgareidge, K., *Ind. Eng. Chem.*, **30**, 839 (1938).

[173] Supplee, G. C., and Dow, O. D., *J. Biol. Chem.*, **75**, 227 (1927); *Am. J. Diseases of Children*, **41**, 1353 (1931); Cannon, H. J., and Hixson, O. F., *Ind. Eng. Chem.*, **28**, 1009 (1936).

[174] See also Schoenleber, F. C., Steenbock, H., and Baumann, C. A., *Wis. Agr. Expt. Sta. Bull. 435*, 66 (1936); *Chem. Abs.*, **32**, 2986 (1938).

[175] British Med. Research Council, *J. Soc. Chem. Ind.*, **48**, 279 (1929); Gorter, E., and Soer, J. J., *Nederland. Tijdschr. Geneesk.*, **74, II**, 4310 (1930); Machti, A., *Pediatria Rivista*, **37**, 1175 (1929); Shohl, A. T., and Bing, F. C., *Am. J. Physiol.*, **86**, 633 (1928); von Noel, L., and Dannmeyer, F., *Strahlentherapie*, **32**, 769 (1929); *Chem. Abs.*, **24**, 4808 (1930); Blunt, K., and Cowen, R., "Ultraviolet Light and Vitamin D. in Nutrition," Univ. of Chicago Press, 1930.

It has been demonstrated by Hume, Lucas and Smith[176] that vitamin D from irradiated cholesterol can be absorbed from a small area of undamaged skin in amounts sufficient to supply the needs of the rat and rabbit. Similar results have been recorded by Astrowe and Morgen,[177] by Fodor,[178] by Amrhein,[179] and by Helmer and Jansen.[180]

The demonstration that the vitamin is absorbed from the skin and the assumption that it may exert a beneficial effect on the skin have prompted many proposals for its local application. Lorenz and Wodlinger[181] incorporate an irradiated sterol in toilet soap during crutching or milling. Cholesterol, phytosterol, zymosterol, etc. were irradiated with x-rays, infrared rays or cathode rays. Wearham[182] adds ergosterol to the soap or to the fats to be saponified and irradiates the mixture.

In a cosmetic skin cream, Goodall[183] proposed the use of cottonseed oil which had been treated with ultraviolet rays along with a mineral oil and a waxy substance. Apparatus for irradiating wool fat or wool-fat alcohols for use in cosmetic creams has been described.[184]

Autolyzed yeast, mixed with organic solvents and irradiated, has been proposed for use in treating the skin.[185]

[176] Hume, E. M., Lucas, N. S., and Smith, H. H., *Biochem. J.*, **21**, 362 (1927).

[177] Astrowe, P. S., and Morgen, R. A., *Am. J. Diseases Children*, **49**, 912 (1935); *Chem. Abs.*, **29**, 5158 (1935).

[178] Fodor, M. E., *Z. Vitaminforschung*, **3**, 241 (1934); *Chem. Abs.*, **29**, 5487 (1935).

[179] Amrhein, F. J., *J. Am. Pharm. Assoc.*, **22**, 182 (1934); *Chem. Abs.*, **28**, 5505 (1934). For a review, see Schuler, R., *Drug and Cosmetic Industry*, **38**, 485 (1936).

[180] Helmer, A. C., and Jansen, C. H., *Studies Inst. Divi Thomae*, **1**, 83, 99 (1937).

[181] Lorenz, A. J., and Wodlinger, M. H., British P. 403,083, June 10, 1932; *Chem. Abs.*, **28**, 3261 (1934); French P. 742,181, March 1, 1933; *Chem. Abs.*, **27**, 3632 (1933); Lorenz, A. J., U. S. P. 2,060,228 (to Lever Bros.); *Chem. Abs.*, **31**, 566 (1937).

[182] Wearham, J., British P. 403,650, Dec. 20, 1933; *Chem. Abs.*, **28**, 3261 (1934).

[183] Goodall, F. E., U. S. P. 1,636,814, May 3, 1927; *Chem. Abs.*, **21**, 2171 (1927).

[184] Leo-Werke, German P. 622,373, Nov. 27, 1935; Austrian P. 137,455, May 11, 1934.

[185] Baeder Illatszergyár, R. T., Hungarian P. 114,585; July 1, 1936; *Chem. Abs.*, **30**, 7284 (1936).

Chapter 41

Ultraviolet Light and Other Vitamins

Although some have suggested that vitamins other than D may also be produced by the irradiation of precursors,[1] no evidence exists for such processes. Suggestions have been made repeatedly that the formation of vitamins, particularly A and C, is in some manner related to the processes of photosynthesis.[2]

Too little is yet known of the mechanism of the photosynthetic formation of carbohydrates for definite statements to be made regarding a possible participation of either vitamin A or C, but the evidence as yet available is not very strongly in favor of this viewpoint.

Measurements of the ultraviolet absorption spectra of vitamin concentrates have significantly aided in the isolation and identification of the vitamins, and studies of the destruction of the purified compounds during irradiation have led to definite results.

Vitamin C. Reyher and Meller [3] observed that a prolonged irradiation of milk with exclusion of air causes some loss in its antiscorbutic properties. When irradiated in an open vessel under conditions in which ozone may be formed, there is a complete destruction of the vitamin. The loss which occurs in the practical irradiation of milk for the production of vitamin D is not important.[4] Booth and Kon [5] observed that milk which originally gave the vitamin C test based upon the reduction of the indophenol reagent, failed to do so after direct exposure to sunlight. Treatment for an hour with hydrogen sulfide restored 90 per cent of the original reducing value. The non-restorable loss increased with the duration of the exposure, so that after six hours only 50 per cent could be restored by the hydrogen sulfide treatment. The destruction follows a unimolecular course. The destruction in milk may be photosensitized by lactoflavin.[6] Indeed, Hopkins maintains that in pure buffered solutions at pH 7.4, ascorbic acid is stable in sunlight, although it is rapidly oxidized in the presence of small amounts of lactoflavin.[7] Ultraviolet light, however, causes a decomposition of *l*-ascorbic acid, even in the absence of oxygen.[8] This change is also accelerated by lactoflavin, but is retarded by acid. Dehydroascorbic acid could not be detected in the products formed. This oxidized form is not affected by irradiation.

Milanesi [9] failed in attempts to increase the amount of this vitamin in oats by irradiation and concluded that it was destroyed or altered by the treatment.

[1] Bowden, F. P., and Snow, C. P., *Nature*, **129**, 720 (1932).

[2] Heller, V. G., and St. Julian, R. R., *J. Nutrition*, **4**, 227 (1931); *Chem. Abs.*, **25**, 5915 (1931); Heller, V. G., *J. Biol. Chem.*, **76**, 499 (1928); Crist, J. W., and Dye, M., *Ibid.*, **91**, 127 (1931); Smith, L. L. W., and Morgan, A. F., *Ibid.*, **101**, 43 (1933).

[3] Reyher, P., and Meller, B., *Klin. Wochschr.*, **5**, 2341 (1926); *Chem. Abs.*, **21**, 2149 (1927).

[4] Hottinger, A., *Klin. Wochschr.*, **6**, 1793 (1927); *Chem. Abs.*, **22**, 798 (1928); Supplee, G. C., and Dow, O. D., *Am. J. Diseases of Children*, **41**, 1353 (1931).

[5] Booth, R. G., and Kon, S. K., *Nature*, **134**, 936 (1934); Kon, S. K., and Watson, M. B., *Biochem. J.*, **30**, 2273 (1936).

[6] Hand, D. B., Guthrie, E. S., and Sharp, P. F., *Science*, **87**, 439 (1938).

[7] Hopkins, F. G., *Compt. rend. trav. lab. Carlsberg, Sér. chim.*, **22**, 226 (1938); *Chem. Abs.*, **32**, 6265 (1938).

[8] Kellie, A. E., and Zilva, S. S., *Biochem. J.*, **32**, 1561 (1938).

[9] Milanesi, E., *Boll. soc. ital. biol. sper.*, **3**, 240 (1928); *Chem. Abs.*, **22**, 3911 (1928).

Cultrera [10] found the reducing factor of lemon juice to be destroyed by Wood's light. According to v. Euler and Klussmann,[11] the optical activity of hexuronic acid decreases when it is kept in a current of oxygen under ultraviolet rays. Ascorbic acid is now known to have an absorption maximum at 2600A in water and at 2630 to 2650A in alcohol.[12]

Eggleton and Harris [13] conclude that light is unnecessary for the natural synthesis of this vitamin. Irradiation of infant food did not increase its content of ascorbic acid. Mercury-arc irradiation of cabbage in which the vitamin had been destroyed by heat gave but a doubtful regeneration. Irradiation has no curative action on scorbutic animals.[14] Heller [15] has claimed that the formation of vitamin C (and also A), although it occurs during the germination and early growth of seedlings in darkness, is accelerated by exposure to light. Similar observations have since been reported by Matsuoka [16] and by Lee and Read.[17] Virtanen and Eerola [18] tend to ascribe such results to an effect of temperature rather than light, at least in the case of the pea.

It has been claimed that a brief irradiation by ultraviolet light of the skin of a guinea pig increases its ascorbic acid content, although a longer one (25 minutes) decreases it.[19]

The claim of Rygh [20] that vitamin C could be obtained by the irradiation of narcotine derivatives has since been refuted.[21] It appears to have been based upon unsuitable biological testing of the irradiation product.

Several observers have noted irradiation, particularly with visible light in the presence of a photosensitizer such as methylene blue, to lower the redox potential of ascorbic acid.[22] It has been proposed to take advantage of this property in a method for the assay of ascorbic acid in tissues.[23] Cornbleet [24] finds irradiation of skin to lower its ascorbic acid content. Pigmented skin has more ascorbic acid than fair skin. Buruianâ believes it possible to determine the vitamin C content of milk by comparing the reduction of iodine before and after the exposure of the milk to sunlight.[25]

[10] Cultrera, R., *Ind. ital. conserve aliment.*, **9**, 9 (1934); *Chem. Abs.*, **28**, 3763 (1934).

[11] v. Euler, H., and Klussmann, E., *Svensk Kem. Tid.*, **44**, 290 (1932); *Chem. Abs.*, **27**, 4566 (1933).

[12] Herbert, R. W., and Hirst, E. L., *Nature*, **130**, 205 (1932); *Biochem. J.*, **29**, 1881 (1935); Bowden, F. P., and Snow, C. P., *Nature*, **129**, 720 (1932); Karrer, P., Schwarzenbach, G., and Schöpp, K., *Helv. Chim. Acta*, **16**, 181 (1933); Robertson, E. B., *J. Soc. Chem. Ind.*, **53**, 277 (1934); Plaut, F., Bülow, M., and Pruckner, F., *Z. physiol. Chem.*, **234**, 131 (1935).

[13] Eggleton, P., and Harris, L. J., *Brit. Med. J.*, **II**, 989 (1925); *Chem. Abs.*, **20**, 1651 (1926).

[14] Holtz, P., and Wöllpert, K., [*Arch. Exptl. Path. Pharmakol.*, **182**, 164 (1936)] believed it to cause some delay in the onset of scurvy.

[15] Heller, V. G., *J. Biol. Chem.*, **76**, 499 (1928).

[16] Matsuoka, T., *Mem. Coll. Agr. Kyoto Imp. Univ.*, **24**, 37 (1932); **35**, 93 (1935); *Chem. Abs.*, **27**, 2180 (1933); **30**, 139 (1936); *J. Agr. Chem. Soc. Japan*, **9**, 81 (1933); **12**, 1203 (1936); *Chem. Abs.*, **31**, 3103 (1937).

[17] Lee, Wei-Yung, and Read, B. E., *J. Chinese Chem. Soc.*, **4**, 208 (1936); *Chem. Abs.*, **31**, 430 (1937). See also Tsuge, H., and Kurihara, K., *Sei-i-kai Med. J.*, **56**, No. 6, 894 (1937); *Chem. Abs.*, **31**, 8610 (1937); Randoin, L., Giroud, A., and Ratsimamanga, R., *Compt. rend. soc. biol.*, **126**, 1068 (1937); *Chem. Abs.*, **32**, 2570 (1938).

[18] Virtanen, A. I., and Eerola, L. V., *Suomen Kemistilehti*, **9B**, 13 (1936); *Chem. Abs.*, **31**, 2254 (1937). See, however, Veselkin, N. V., Lyubimenko, V. N., Bulgakosa, S. P., Tichalskaya, V. V., and Engel, P. S., *Izv. Nauch. Inst. Lesgafta*, **17**, 389, 405 (1934); *Chem. Abs.*, **31**, 6696 (1937).

[19] Castellini, P., *Giorn. ital. dermatol. sifilol.*, **77**, 967 (1936); *Chem. Abs.*, **32**, 226 (1938).

[20] Rygh, O., Rygh, A., and Laland, P., *Z. physiol. Chem.*, **204**, 105; **211**, 275 (1932).

[21] Westin, G., *Z. Vitaminforsch.*, **2**, 1 (1933); *Chem. Abs.*, **27**, 4560 (1933); Shimada, J., *J. Biochem. Japan*, **17**, 395 (1933); *Chem. Abs.*, **27**, 5103 (1933).

[22] Viale, G., *Rev. sudamer. endocrinol. immunol. quimio-terap.*, **17**, 547 (1934); *Chem. Abs.*, **28**, 6794 (1934); Lund, H., and Lieck, H., *Skand. Arch. Physiol.*, **74**, 269 (1936); Martini, E., *Biochim. terap. sper.*, **20**, 505 (1933); *Chem. Abs.*, **28**, 3456 (1934).

[23] Martini, E., and Bonsignore, A., *Boll. soc. ital. biol. sper.*, **9**, 388 (1934); *Chem. Abs.*, **28**, 6460 (1934); Bonsignore, A., *Boll. soc. ital. biol. sper.*, **10**, 62 (1935); *Chem. Abs.*, **29**, 3385 (1935).

[24] Cornbleet, T., *Arch. Dermatol. Syphilol.*, **35**, 471 (1937); *Chem. Abs.*, **31**, 5412 (1937).

[25] Buruianâ, L., *Biochem. J.*, **31**, 1452 (1937).

Vitamins of the B Group. During the early difficult period when the multiplicity of the water-soluble vitamins other than ascorbic acid was being investigated and when but two such products were definitely recognized, attempts were made, in anticipation of any knowledge of their structure or absorption spectra, to differentially destroy one but not the other by the aid of ultraviolet light. This treatment was intended to be applied to yeast used in experimental diets for the production of deficiencies, the growth factor other than B_1 being the more susceptible.[26] Kennedy and Palmer [27] doubted that such methods could be relied upon, since both factors could be destroyed, but with varying ease. Hogan and Hunter showed that autoclaving had the opposite effect, destroying the antineuritic factor more rapidly than the growth factor. Hogan and Richardson [28] claimed to have attained satisfactory results in the destruction of the antidermatitis factor by mercury-arc irradiation. Guerrant and Salmon [29] found the destruction of the growth-promoting factor to proceed more rapidly when the irradiation was applied to an alkaline solution. After the later recognition of the flavins as growth-promoting factors, Hogan and Richardson [30] reinvestigated the matter and concluded that in irradiation of the diets both the flavins and an unidentified factor essential for the prevention of dermatitis are destroyed. It has since been shown by others that the rat antidermatitis factor is pyridoxine [2-methyl-3-hydroxy-4,5-di-(hydroxymethyl)-pyridine]. In the determination of its structure, ultraviolet absorption spectra gave important information. Nicotinic acid, the antipellagra factor, has an absorption maximum at about 2600A.[31]

Contrary to these observations, Halliday and Evans [32] state that none of the factors present in brewers' yeast extract was destroyed by ten hours of irradiation. Doubtless this result is to be ascribed to the presence of substances in the extracts which act as internal filters. It is now known that B_1 (thiamine), the flavins and nicotinic acid can be destroyed when solutions of the pure substances are irradiated by ultraviolet light (visible light in the case of the flavins). György [33] finds a pellagra-preventing factor to be destroyed by visible light, at the same time changing from yellow to brown.

Before the chemical purification of B_1 concentrates had advanced to a stage in which sulfur was recognized as a constituent of the compound, attempts were made to prepare the vitamin from various precursors. Heyroth and Loofbourow [34] called attention to the resemblance of the ultraviolet absorption spectra of highly purified concentrates to the spectra of purines and pyrimidines and noted that irradiation of the latter with ultraviolet light from which the shorter wave-lengths had been excluded seemed to increase the resemblance. They showed, however,[35] that irradiated nucleic acids and irradiated uracil lacked antineuritic and growth-promoting properties. Guha [36] claimed to have been successful in producing the antineuritic vitamin by the irradiation of adenine. Other workers confirmed the observations of Heyroth that the vitamin

[26] Hogan, A. G., and Hunter, J. E., *J. Biol. Chem.*, **78,** 433 (1928).

[27] Kennedy, C., and Palmer, L. S., *J. Biol. Chem.*, **83,** 493 (1929).

[28] Hogan, A. G., and Richardson, L. R., *Mo. Agr. Exp. Sta. Research Bull., 178,* 3 (1932).

[29] Guerrant, N. B., and Salmon, W. D., *J. Biol. Chem.*, **89,** 199 (1930).

[30] Hogan, A. G., and Richardson, L. R., *Nature,* **136,** 186 (1935); *Science,* 83, 17 (1936); *Mo. Agr. Exp. Sta., Bull. 340,* 26 (1934).

[31] Compare the absorption of a growth-factor called B_2 by Karrer, P., and von Euler, H., *Arch. Kemi, Mineral Geol.*, **11B,** No. 16 (1933); *Chem. Abs.*, **27,** 5101 (1933).

[32] Halliday, N., and Evans, H. M., *J. Biol. Chem.*, **118,** 255 (1937).

[33] György, P., *Biochem. J.*, **29,** 767 (1935).

[34] Heyroth, F. F., and Loofbourow, J. R., *Bull. Basic Science Research,* 3, 237 (1931).

[35] Heyroth, F. F., and Loofbourow, J. R., *Nature,* **131,** 92 (1933); *Bull. Basic Science Research,* 4, 119 (1932).

[36] Guha, B. C., *Nature,* **130,** 741 (1932). Bonner, J., and Greene, J., [*Botan. Gaz.*, **100,** 226 (1938); *Chem. Abs.*, **32,** 9185 (1938)] believe the thiamin content of pea plants increases in light.

cannot be produced by the irradiation of a simple purine or pyrimidine [37] and Guha and Chakravorty [38] later admitted that irradiated adenine does not cure avian polyneuritis, although they still believed it to have growth-promoting properties. This Schultz and Laquer suggest may have been due to a contamination of the adenine used by one of the growth-promoting vitamins of the B group.

Heyroth and Loofbourow [39] later studied samples of crystalline thiamine (B_1) as well as concentrates of varying degrees of purity. It was shown that pure thiamine had absorption maxima at about 2650A and 2350A. Ultraviolet irradiation destroys the physiological activity and reduces the extinction coefficients.[40] An oxidation product, thiochrome, which has an intense fluorescence employed for assay purposes, is rapidly destroyed by ultraviolet light.[41]

Absorption studies and observations of the destructive effects of irradiation with visible light have played an important part in the development of our knowledge of the flavins as growth-promoting vitamins. The brilliant green fluorescence of these materials led to their discovery and guided their isolation. That the flavins in aqueous alkaline solution could be photochemically inactivated by visible light was shown in one of the first papers dealing with these substances.[42]

During this process there was produced a colored substance soluble in chloroform, which came to be known as a lumiflavin or lumichrome.[43]

It was shown by Kuhn and Wagner-Jauregg [44] that the photolysis consists in the splitting off of an oxygen-rich, nitrogen-free group of atoms:

$$\underset{\textit{Lactoflavin}}{C_{17}H_{20}N_4O_6} - C_4H_8O_4 \rightarrow \underset{\textit{Lumilactoflavin}}{C_{13}H_{12}N_4O_2}$$

Other flavins, such as uroflavin, maltoflavin and hepatoflavin were shown to undergo a similar photolysis,[45] which involves the loss of a sugar-like side-chain. In searching for analogies for this behavior, Kuhn and Bär [46] showed that when 2-tetraoxybutylquinoxaline is irradiated in alkaline solution, the tetraoxybutyl residue held on a carbon atom is replaced by an atom of hydrogen with the formation of the chloroform-soluble quinoxaline. In this case, however, the original compound was colorless so that it was necessary to employ ultraviolet light.

Similarly, Ohle [47] found the closely related 3-tetraoxybutyl-2-oxyquinoxaline loses not four but three carbon atoms as glycerin and yields 2-oxyquinoxaline-3-aldehyde. Irradiation of an alkaline solution of pentahydroxyamyl-benzimidazole

[37] Schultz, F., and Laquer, F., *Z. physiol. Chem.*, **219,** 158 (1933); Sure, B., *Biochem. J.*, **27,** 2043 (1933); Yamamoto, R., and Yamagishi, T., *J. Agr. Chem. Soc. Japan,* **9,** 749 (1933); *Chem. Abs.*, **27,** 5381 (1933). It was early shown that irradiation of a polyneuritic animal has no favorable effects. Krizenecky, J., *Arch. ges. Physiol, (Pflüger's),* **204,** 407 (1924); **211,** 663 (1926); *Chem. Abs.*, **20,** 1437 (1926).

[38] Guha, B. C., and Chakravorty, P. N., *Nature,* **132,** 447 (1933); *J. Indian Chem. Soc.*, **11,** 195 (1934); *Chem. Abs.*, **28,** 5503 (1934).

[39] Heyroth, F. F., and Loofbourow, J. R., *Bull. Basic Sci. Research,* **4,** 35 (1932); *Nature,* **134,** 461 (1934); *Biochem. J.*, **30,** 651 (1936); see also Peters, R. A., and Philpot, J., *Proc. Roy. Soc.*, **B113,** 48 (1931); Holiday, E. R., *Biochem. J.*, **29,** 719 (1935); Wintersteiner, O., Williams, R. R., and Ruehle, A. E., *J. Am. Chem. Soc.*, **57,** 517 (1935).

[40] Heyroth, F. F., and Loofbourow, J. R., *J. Am. Chem. Soc.*, **56,** 2010 (1934); Kakefuda, H., *Fukuoka Acta Med.*, **27,** 99 (1934); *Chem. Abs.*, **29,** 6278 (1935).

[41] Otto, H., and Rühmekorb, F., *Klin. Wochschr.*, **17,** 1246 (1938); *Chem. Abs.*, **32,** 9133 (1938).

[42] Kuhn, R., György, P., and Wagner-Jauregg, T., *Ber.*, **66,** 317 (1933).

[43] Ellinger, P., and Koschara, W., *Ber.*, **66,** 808, 1411 (1933).

[44] Kuhn, R., and Wagner-Jauregg, T., *Ber.*, **66,** 1577 (1933); Kuhn, R., Rudy, H., and Wagner-Jauregg, T., *Ber.*, **66,** 1950 (1933).

[45] Stern, K. G., *Nature,* **133,** 178 (1934); Koschara, W., *Z. physiol. Chem.*, **229,** 103 (1934); Bierry, H., and Gouzon, B., *Compt. rend.*, **200,** 2116 (1935); *Chem. Abs.*, **29,** 6911 (1935).

[46] Kuhn, R., and Bär, F., *Ber.*, **67,** 898 (1934).

[47] Ohle, H., *Ber.*, **67,** 155 (1934).

gives a small amount of benzimidazole; the main photochemical product was not identified.[48]

It was later shown by Kuhn and Rudy [49] that during the loss of the sugar-like side-chain in the photolysis of the flavin an alkyl group becomes attached to a nitrogen atom. After much further work, it has been shown that lumilactoflavin is 6,7,9-trimethylisoalloxazine.[50]

In work on the synthesis of substances similar to lactoflavin, Karrer, Schlittler, Pfaehler and Benz [51] noted that their synthetic 9-(betahydroxyethyl) isoalloxazine when irradiated by sunlight in neutral solution gave 9-methylisoalloxazine. In alkaline solution, irradiation gave alloxazine and its 9-methyl derivative. Lumichrome was also obtained from ovoflavin *e* [52] and lactoflavin.[53] Karrer attributes the light-sensitivity of lactoflavin to the presence of a single β- hydroxyl group in the sugar-like side-chain.

When a synthetic branched-chain flavin, 9-(2′,3′-dihydroxy-1′-isopropyl)-isolloxazine, is illuminated in water or methanol solution, it slowly breaks down yielding some alloxazine, the decomposition appearing to start at the hydroxyl in the 2′ position of the side-chain. In alkaline solution, however, easily soluble colorless compounds were formed by the action of light, and no alloxazine could be detected.[54] The decomposition by sunlight of a flavin containing a tertiary hydroxyl group, such as 9-(2′-hydroxy-2′-methyl-1′-propyl) isoalloxazine, however, shows [55] that it is not necessary that dehydrogenation occur at the 2′ position of the hydroxy side-chain. The rate of decomposition is much slower with this compound than with flavins containing a primary or a secondary group. As with the other flavins, the photolysis proceeds more rapidly in aqueous methanol than in water.

Subsequently, Karrer, Köbner, Salomon and Zehender [56] drew more clearly the distinction between the decomposition of lactoflavin to lumichrome (that is, alloxazine) derivatives which occurs in neutral solutions and that of 9-γ-hydroxypropyl isoalloxazine, which fails to react in neutral solutions but is rapidly decomposed to alloxazine in alkaline solutions. The former reaction is said to be a dehydration commencing by oxidation at the β-CHOHCO.[57]

Flavins may exert a photosensitizing action upon ascorbic acid since its oxidation potential falls in light more rapidly in their presence than in their absence.[58]

The brilliant fluorescence of the flavins has been employed in this essay,[59] and practical rapid methods for the application of the Fluoray lamp to the assay of flavins in milk have been given by Whitnah, Kunerth and Kramer [60] and by Supplee, Ansbacher, Flanigan and Hanford.[61]

[48] Kuhn, R., and Bär, F., *Ber.*, **67B**, 898 (1934); Kuhn and Weygand, F., *Ber.*, **67B**, 1939 (1934).

[49] Kuhn, R., and Rudy, H., *Ber.*, **67**, 1298 (1934).

[50] Kuhn, R., Reinemund, K., and Weygand, F., *Ber.*, **67**, 1460 (1934); Kuhn, R., and Rudy, H., [*Ber.*, **67B**, 1936 (1934)] state that lumichrome, similarly formed by irradiation in neutral or acid solutions is 6,7-dimethylalloxazine.

[51] Karrer, P., Schlittler, E., Pfaehler, K., and Benz, F., *Helv. Chim. Acta*, **17**, 1516 (1934).

[52] Karrer, P., and Schöpp, K., *Helv. Chim. Acta*, **17**, 1557 (1934).

[53] Karrer, P., Salomon, H., Schöpp, K., Schlittler, E., and Fritzsche, H., *Helv. Chim. Acta*, **17**, 1010 (1934).

[54] Karrer, P., and Meerwein, H., *Helv. Chim. Acta*, **18**, 480 (1935).

[55] Karrer, P., and Meerwein, H., *Helv. Chim. Acta*, **18**, 1126 (1935).

[56] Karrer, P., Köbner, T., Salomon, H., and Zehender, F., *Helv. Chim. Acta*, **18**, 266 (1935).

[57] For further details concerning the structure of related compounds as affecting the photolysis, see, Karrer, P., and Musante, C., *Helv. Chim. Acta*, **18**, 1134 (1935); Karrer, P., Köbner, T., and Zehender, F., *Ibid.*, **19**, 261 (1936); Karrer, P., and Naef, R., *Ibid.*, **19**, 1029 (1936).

[58] Martini, E., *Boll. soc. ital. soc. biol. sper.*, **9**, 1235 (1934); *Chem. Abs.*, **29**, 2580 (1935); Süllmann, H., *Klin. Wochschr.*, **17**, 1157 (1938); *Chem. Abs.*, **32**, 8273 (1938).

[59] Josephy, B., *Acta Brevia Neerland. Physiol. Pharmacol, Microbiol.*, **4**, 46 (1934); *Chem. Abs.*, **29**, 3362 (1935); Cohen, F. H., *Acta Brevia Neerland. Physiol. Pharmacol. Microbiol.*, **4**, 46 (1934); **5**, 18 (1935); *Chem. Abs.*, **29**, 4044, 4790, 5482 (1935); *Rec. trav. chim.*, **54**, 133 (1935); Bierry, H., and Gouzon, B., *Compt. rend. soc. biol.*, **119**, 101 (1935); *Chem. Abs.*, **29**, 5133 (1935); Karrer, P., and Fritzsche, H., *Helv. Chim. Acta*, **18**, 911 (1935); van Eekelen, M., and Emmerie, A., *Acta Brevia Neerland. Physiol. Pharmacol. Microbiol.*, **5**, 77 (1935); Weisberg, S. M., and Levin, I., *Ind. Eng. Chem. (Anal. Ed.)*, **9**, 523 (1937).

[60] Whitnah, C. H., Kunerth, B. L., and Kramer, M. M., *J. Am. Chem. Soc.*, **59**, 1153 (1937).

[61] Supplee, G. C., Ansbacher, S., Flanigan, G. E., and Hanford, Z. M., *J. Dairy Sci.*, **19**, 215 (1936).

It must also be noted that the methods of irradiation which proved so helpful in the study of the constitution of the flavins had in fact been based upon similar previous observations of the behavior of a yellow oxidation enzyme obtained from yeast by Warburg and Christian,[62] and which contains a flavin prosthetically bound to a protein. Observations by Theorell [63] show that so long as the active group (flavin phosphate) is combined with protein, it is unchanged by light, but when liberated in alkaline solution it behaves like lactoflavin. The destruction of the flavin or its ester proceeds more rapidly in the presence of oxygen than in its absence, but more rapidly in air than in pure oxygen. In an argon atmosphere, deuteroleucoflavin phosphate is first formed, and on continued irradiation in the absence of oxygen slowly splits to 6,7-dimethylalloxazine; on the admission of air, however, the unchanged leuco- compound is at once oxidized to deuteroflavin phosphate, which is rapidly split to dimethylalloxazine by light. Therefore, in the presence of air the deuterocompounds are not formed. In a strongly alkaline medium, the deuteroflavin is changed quantitatively to lumiflavin without the formation of dimethylalloxazine.

Vitamin A. Absorption spectrum studies have played a large part in the study of the constitution of vitamin A, as well as that of carotene which may replace it in the diet, being converted into the vitamin in the liver.[64]

Morton and Heilbron [65] showed that vitamin A concentrates exhibit a prominent absorption band at 3285A, the intensity of which accords with the potency as determined by the depth of a blue color produced by antimony trichloride. In some fish oils, however, as in dogfish oil, the characteristic absorption band may be masked by absorption bands due to other substances. General confirmation of the absorption of the vitamin at 3280A was given by Drummond and Morton.[66] Evidence has been brought forward recently for the existence in the livers of certain fresh-water fishes of a second vitamin A, A_2, with an absorption maximum displaced to 3450-3500A.[67]

The Hilger Vitameter has been introduced to facilitate the assay of vitamin A by measuring the 3280A band.[68] In the development of absorption assay methods

[62] Warburg, O., and Christian, W., *Naturwiss.*, **20**, 980 (1932); *Biochem. Z.*, **258**, 496 (1933); British P. 430,571, June 17, 1935; *Chem. Abs.*, **29**, 7362 (1935).

[63] Theorell, H., *Biochem. Z.*, **279**, 186 (1935).

[64] Morton, R. A., "Applications of Absorption Spectra to the Study of Vitamins and Hormones," London, A. Hilger, Ltd.; Chevallier, A., *Bull. soc. chim. biol.*, **17**, 530 (1935); Rosenthal, J., and Weltner, M., *Biochem. J.*, **29**, 1036 (1935); De, N. K., *Indian J. Med. Research*, **22**, 509 (1935).

[65] Morton, R. A., and Heilbron, I. M., *Nature*, **122**, 10 (1928); *Biochem. J.*, **22**, 987 (1928).

[66] Drummond, J. C., and Morton, R. A., *Biochem. J.*, **23**, 785 (1929). Morton, R. A., Heilbron, I. M., and Spring, F. S., [*Biochem. J.*, **24**, 136 (1930)] answer certain objections raised by Rosenheim, O., and Webster, T. A., *Ibid.*, **23**, 633 (1929). See also Woodrow, J. W., and Cunningham, H. L., *Phys. Rev.*, **35**, 125 (1930); Woodrow, J. W., and Philipson, J. B., *Proc. Iowa Acad. Sci.*, **37**, 310 (1930); Coward, K. H., Dyer, F. J., and Morton, R. A., *Biochem. J.*, **26**, 1593 (1932); Chevallier, A., and Chabre, P., *Biochem. J.*, **27**, 298 (1933); Josephy, B., *Acta Brevia Neerland. Physiol. Pharmakol. Microbiol.*, **3**, 133 (1933); *Chem. Abs.*, **28**, 2467 (1934); Crews, S. K., and Cox, S. J., *Analyst*, **59**, 85 (1934); *Chem. Abs.*, **28**, 2756 (1934).

[67] Gillam, A. E., Heilbron, I. M., Lederer, E., and Rosanova, V., *Nature*, **140**, 233 (1937); Edisbury, J. R., Morton, R. A., and Simpkins, G. W., *Ibid.*, **140**, 234 (1937); Lederer, E., and Rathmann, F. H., *Biochem. J.*, **32**, 1252 (1938). Compare Chevallier, A., and Choron, Y., [*Compt. rend., soc. biol.*, **127**, 1443 (1938); *Chem. Abs.*, **32**, 6298 (1938)] who distinguish hemo- and hepato-forms of vitamin A.

[68] French P. 760,676, Feb. 28, 1934, to Adam Hilger Ltd.; *Chem. Abs.*, **28**, 4180 (1934); British P. 416,423, Sept. 19, 1934; Twyman, F., and Follet, D. H., U. S. P. 2,065,953, Dec. 29, 1936, to Adam Hilger Ltd.; *Chem. Abs.*, **31**, 911 (1937); Irish, F. W., *J. Assoc., Off. Agr. Chem.*, **19**, 244 (1936); Wilkie, J. B., *Ibid.*, **20**, 208 (1937); Notevert, O., *Biochem. J.*, **29**, 1227 (1935); Baumann, C. A., and Steenbock, H., *J. Biol. Chem.*, **101**, 547 (1933); Baumann, C. A., Steenbock, H., Beeson, W. M., and How, T. G., *Can. J. Research*, **13A**, 93 (1935); McFarlane, W., and Rudolph, L., *Sci. Agr.*, **16**, 398 (1936); *Chem. Abs.*, **30**, 6405 (1936); Rupel, I. W., *Ibid.*, **105**, 167 (1934); Shrum, G. H., and Holmes, A. D., Black, A., Barthen, C. L., and Leonard, C. S., *J. Am. Pharm. Assoc.*, **26**, 515 (1937); Holmes, A. D., Black, A., Eckler, C. R., Emmett, A. D., Heyl, F. W., Neilsen, C. and Quinn, E. J., *Ibid.*, **26**, 525 (1937); *Chem. Abs.*, **31**, 6274 (1937); Nijveld, W. J., *Chem. Weekblad*, **34**, 379 (1937); *Chem. Abs.*, **31**, 7461 (1937); Leech, W. D., *Australian Chem. Inst. J. and Proc.*, **5**, 155 (1938); *Chem. Abs.*, **32**, 6281 (1938); McFarlan, R. L., and Reddie, J. W., U. S. P. 2,123,573, July 12, 1938; *Chem. Abs.*, **32**, 6510 (1938).

account must be taken of the absorption of carotene since that substance is physiologically equivalent to the vitamin. Its absorption spectrum is different,[69] lacking the band at 3280A. It has bands between 3300 and 3400A and between 2630 and 2950A.[70] The discovery of the conversion of carotene into vitamin A in the liver has been followed by spectrographic methods. Capper [71] showed that the liver oil of rats deficient in vitamin A lacked its characteristic 3280A band and that this was present in the liver oil of rats which had been cured by the administration of carotene. Basu [72] suggested that this change can occur only in animals receiving ultraviolet radiations. Bowden and Snow [73] believed that irradiation of β-carotene in cyclohexane produces a change in the absorption spectrum indicative of the production of vitamin A, but Dann [74] believes that this is precluded by the fact that the vitamin is more rapidly destroyed than is carotene by the 2650A line.

The extensive work on the assay of vitamin A by the spectrophotometric measurement of the intensities of colors produced on the addition of antimony trichloride lies beyond the scope of our present discussion.

The photochemical destruction of vitamin A has been very extensively studied. Earlier divergent findings were in large part due to the use of the antimony trichloride method, the results being somewhat masked by the effects of the several other chromogens which may accompany the vitamin in the oils and concentrates studied. It was first observed by Peacock [75] that the exposure of cod-liver oil to white light caused a loss of its fluorescence and of its ability to give the arsenic trichloride test then employed for the determination of the vitamin. The ability of the oil to promote growth in rats was lost. Confirmations were reported by Holmes and Pigott [76] and Titus, Hughes, Hinshaw and Fitch [77] stated that the irradiation of milk by a mercury arc caused a loss of some vitamin A. Zilva [78] reported that the irradiation of butter with ultraviolet light did not lead to the production of toxic substances as had been reported by Spinka.[79]

Willimot and Wokes [80] irradiated cod-liver oil in an open dish only three inches from a mercury arc, the temperature rising to 70° in 90 minutes. One third of the vitamin A, determined by the colorimetric method, was destroyed in the first hour and the whole of it in two hours. They also noted that after a few minutes of irradiation, a slow destruction of the vitamin continued for a long period. Morton and Heilbron [81] confirmed the results by noting the disappearance of the band

[69] Morton, R. A., and Heilbron, I. M., *Biochem. J.*, **24**, 870 (1930); Kawakami, K., *J. Agr. Chem. Soc. Japan*, **8**, 48 (1932); *Chem. Abs.*, **27**, 1661 (1933); Smith, J. H. C., *J. Am. Chem. Soc.*, **58**, 247 (1936).

[70] See also Woodrow, J. W., and Philipson, J. B., *Proc. Iowa Acad. Sci.*, **38**, 218 (1931); *Chem. Abs.*, **27**, 2184 (1933); Winterstein, A., *Z. physiol. Chem.*, **215**, 51 (1933); von Euler, H., and Klussmann, E., *Arkiv Kemi, Mineral. Geol.*, **11B**, No. 17 (1933); Miller, E. S., *Plant Physiol.*, **9**, 179 (1934); *Bot. Gaz.*, **96**, 447 (1935); *Plant Physiol.*, **10**, 375 (1935); Karrer, P., and Solmssen, U., *Helv. Chim. Acta*, **18**, 25 (1935); Castle, D. C., Gillam, A. E., Heilbron, I. M., and Thompson, H. W., *Biochem. J.*, **28**, 1702 (1934). Carotene may be bleached by ultraviolet rays in treating cream for butter-making, according to H. E. Kistner, U. S. P. 2,119,461, May 31, 1938; *Chem. Abs.*, **32**, 5526 (1938).

[71] Capper, N. S., *Biochem. J.*, **24**, 980 (1930).

[72] Basu, N. K., *Z. Vitaminforschung*, **3**, 254 (1934); *Chem. Abs.*, **29**, 5487 (1935).

[73] Bowden, F. P., and Snow, C. P., *Nature*, **129**, 720 (1932).

[74] Dann, W. J., *Biochem. J.*, **27**, 274 (1933); see also De, N. K., *Indian J. Med. Research*, **23**, 505 (1935).

[75] Peacock, P. R., *Lancet*, **II**, 328 (1926); *Science*, Oct. 15, **1926.**

[76] Holmes, A. D., and Pigott, M. G., *Boston Med. Surg. J.*, **195**, 263 (1926).

[77] Titus, R. W., Hughes, J. S., Hinshaw, W. R., and Fitch, J. S., *Ind. Eng. Chem.*, **18**, 843 (1926).

[78] Zilva, S. S., *Biochem. Z.*, **155**, 333 (1925).

[79] Spinka, J., *Biochem. Z.*, **153**, 197 (1924).

[80] Willimot, S. G., and Wokes, F., *Pharm. J.*, **118**, 217 (1927); *Chem. Abs.*, **21**, 3220 (1927); *Lancet*, **II**, 8 (1927); *Chem. Abs.*, **22**, 257 (1928).

[81] Morton, R. A., and Heilbron, I. M., *Nature*, **122**, 10 (1928).

at 3280A. Their absorption studies indicated that the first decomposition products of the vitamin might possess an absorption band in the region 2750 to 2850A. A very rich shark-liver oil was employed. Steenbock and Wirick [82] found the destruction of the vitamin in butter-fat to be proportional to the time of irradiation and inversely proportional to the thickness of the layer exposed. The process could be retarded by surrounding the fat with an inert gas.

Norris [83] used both colorimetric and biological assays and conducted the irradiation of cod-liver oil in a rotating closed quartz cylinder under carbon dioxide, at a temperature not over 15°C. Preliminary work indicated an induction period of about two hours, although in subsequent experiments [84] this could be confirmed only for the biological assays. A plot of the reciprocals of the chromogen which with antimony trichloride gives absorption between 600 and 617 mμ against the time of exposure gave a straight line. The vitamin content reached zero after about four hours.

By colorimetric determinations, Evers [85] found little or no change in the first two hours, after which there was a slow change. Hawk [86] reported an actual increase in the antimony trichloride blue color during irradiation in air. Although denied by Drummond,[87] this observation was confirmed by Norris and Church [88] and by Heilbron, Gillam and Morton.[89]

Wave-lengths shorter than 3350 to 3400A are required for the destruction of the vitamin.[90]

Chevallier [91] found carbon-arc irradiation of a hexane solution of an unsaponifiable vitamin A concentrate to produce a rapid destruction of the absorption band at 3280A. At the same time there was evidence from the absorption changes within the region 2900 to 3400A [92] of the production of new products which in turn were destroyed at different rates. One product formed may be an intermediate between vitamin A and β-ionone.[93] From the results of the use of filtered light of 3650A Chevallier and Dubouloz [94] calculated the quantum yield as 1/28, and noted that the decomposition follows a somewhat different course in slightly acid and in slightly alkaline ethanol. It is claimed that the formation of several decomposition products may be recognized by analysis of the spectrographic results.[95]

[82] Steenbock, H., and Wirick, A. M., *J. Dairy Sci.*, **14**, 229 (1931); *Chem. Abs.*, **25**, 4030 (1931); Shrewsbury, C. L., and Kraybill, H. R., *Science*, **75**, 86 (1932).

[83] Norris, R. J., *Bull. Basic Sci. Research*, **3**, 89 (1931).

[84] Nabarro, D., and Hickman, J. O., found no change in thirty seconds, *Lancet*, **I**, 127 (1930).

[85] Evers, N., *Quart. J. Pharm.*, **2**, 556 (1929); *Brit. Chem. Abs.*, **A**, 1203 (1929).

[86] Hawk, P. B., *Science*, **69**, 200 (1929).

[87] Drummond, J. C., *J. Soc. Chem. Ind.*, **49**, 285T (1930).

[88] Norris, E. R., and Church, A. E., *J. Biol. Chem.*, **89**, 421 (1930).

[89] Heilbron, I. M., Gillam, A. E., and Morton, R. A., *Biochem. J.*, **25**, 1352 (1931). Even the 3280A band increases during the first few minutes of irradiation, according to Boyle, E., *Nature*, **133**, 798 (1934); *Biochem. J.*, **28**, 573 (1934). See also Smith, E. L., Stern, B. E., and Young, F. E., [*Nature*, **141**, 551 (1938)] who find that irradiation sometimes increases and sometimes decreases the absorption, which, however, returns to normal on standing in the dark. These changes may be due to *cis-trans* isomerization. Morton, R. A., *Nature*, **141**, 552 (1938).

[90] Norris, R. J. and Loofbourow, J. R., *Bull. Basic Sci. Research*, **4**, 113 (1932).

[91] Chevallier, A., *Compt. rend. soc. biol.*, **112**, 1681 (1933); *Chem. Abs.*, **27**, 3974 (1933).

[92] Chevallier, A., and Choron, Y., *Compt. rend. soc. biol.*, **115**, 1297 (1934); *Chem. Abs.*, **28**, 4455 (1934).

[93] Chevallier, A., Choron, Y., and Guillot, J., *Compt. rend. soc. biol.*, **117**, 10 (1934); *Chem. Abs.*, **29**, 201 (1935).

[94] Chevallier, A., and Dubouloz(P., *Bull. soc. chim. biol.*, **18**, 190, 703 (1936); *Brit. Chem. Abs.*, **A**, 1159 (1936).

[95] Chevallier, A., Dubouloz, P. and Manuel, S., *Compt. rend. soc. biol.*, **121**, 1415 (1936); Dubouloz, P., *J. chim. phys.* **33**, 532 (1936); Chevallier A. and Dubouloz, P., *Bull. soc. chim. biol.*, **18**, 1115 (1936).

Chevallier uses the changes in absorption at 3250A during irradiation in a method for the spectrographic assay for vitamin A.[96]

Dried spinach loses 70 per cent of its vitamin A during fifteen months of storage in diffused light. Ultraviolet light also decolorizes a petroleum ether extract of carrots and destroys its vitamin A action.[97] Alfalfa leaves bleached in sunlight also show a loss of vitamin A.[98] The same is true of ghee.[99]

The decolorization of carotene is also accelerated by ultraviolet light[100] and it may be this which is changed in alfalfa.[101] Some observations on the photo-öxidation of α-carotene in ultraviolet light, reported by Baur,[102] indicate an induction period, after which the course of the oxygen uptake in chloroform solution is autocatalytic. There may be a reversible formation of a photo-oxide. The changes in absorption spectra of carotene and xanthophyll have been followed during their slow oxidation by McNicholas.[103]

Kuhn and Winterstein[104] have isolated from saffron a dimethyl ester of a substance isomeric with crocetin. It is converted into crocetin by the action of blue or violet, but not of red, light. Radiations of wave-lengths less than 4150A are not essential to the reaction. The isomerization may be of the *cis-trans* type.

Vitamin E.[105] Ultraviolet irradiation destroys absorption bands at 2860 to 3200A at the same time that the activity of a concentrate is diminished, according to Bowden and Moore.[106] Bands at 2400 to 2850A are unaltered. The association of a band at 2940A with the biological activity is confirmed by Drummond, Singer and MacWalter,[107] who also find it to be diminished by irradiation. Olcott,[108] however, believes this band due not to the vitamin but to some closely related, difficultly removable substance.

Extracts of the antihemorrhagic vitamin retain their potency after 24 hours of exposure in a sealed tube to the light of a 500-watt lamp at three to four inches.[109] Later, Almquist[109a] showed direct sunlight to destroy the vitamin.

The protective factor against nutritional encephalomalacia in chicks is also resistant to ultraviolet irradiation.[110]

Photochemistry of Vision.

It is only possible to note briefly that there has recently been a growing interest in the mechanism of vision. The photochemical changes involved are believed to

[96] Chevallier, A., *Z. Vitaminforsch.*, **7,** 10 (1938); *Chem. Abs.*, **32,** 5016 (1938).

[97] Quinn, E. J., Hartley, J. G., and Derow, M. A., *J. Biol. Chem.*, **89,** 657 (1930).

[98] Smith, M. C., and Briggs, I. A., *J. Agr. Research,* **46,** 229, 235 (1933); *Chem. Abs.*, **27,** 235 (1933); Douglass, E., Tobiska, J. W., and Vail, C. E., *Colorado Agr. Exp. Sta., Tech. Bull.* **4,** 68pp. (1933); *Chem. Abs.*, **28,** 3449 (1934).

[99] Banerjee, B. N., and Dastur, N. N., *Agr. Live-Stock, India,* **6,** 433 (1936); *Chem. Abs.*, **31,** 471 (1937).

[100] Olcovich, H. S., and Mattill, H. A., *J. Biol. Chem.*, **91,** 105 (1931); *Chem. Abs.*, **25,** 3697 (1931).

[101] Russell, W. C., Taylor, M. W., and Chichester, D. F., *New Jersey Agr. Exp. Sta. Bull. 560,* 1 (1934); *Chem. Abs.*, **28,** 6788 (1934).

[102] Baur, E., *Helv. Chim. Acta,* **19,** 1210 (1936); **20,** 402 (1937).

[103] McNicholas, H. J., *Bur. Standards J. Research,* **7,** 171 (1931).

[104] Kuhn, R., and Winterstein, A., *Ber.* **66B,** 209 (1933).

[105] For tentative absorption spectra, Bowden, F. P., and Moore, T., *Nature,* **121,** 512 (1933); von Euler, H., Hellström, H., and Klussmann, E., *Svensk Kem. Tid.*, **45,** 132 (1933); *Chem. Abs.*, **27,** 4284 (1933); Morton, R. A., and Edisbury, J. R., *Nature,* **131,** 618 (1933); Martin, A., Moore, T., Schmidt, M., and Bowden, F. P., *Ibid.*, **134,** 214 (1934).

[106] Bowden, F. P., and Moore, T., *Nature,* **132,** 204 (1933).

[107] Drummond, J. C., Singer, E., and MacWalter, R. J., *Biochem. J.*, **29,** 456 (1935).

[108] Olcott, H. S., *J. Biol. Chem.*, **110,** 695 (1935).

[109] Almquist, H. J., *J. Biol. Chem.*, **114,** 241 (1936).

[109a] Almquist, H. J., *J. Biol. Chem.*, **117,** 517 (1937); MacCorquodale, D. W., Binkley, S. B., McKee, R. W., Thayer, S. A., and Doisy, E. A., *Proc. Soc. Exptl. Biol. Med.*, **40,** 482 (1939).

[110] Goettsch, M., and Pappenheimer, A. M., *J. Biol. Chem.*, **114,** 673 (1936).

occur in substances in two different histological structures, the rods scattered throughout much of the retina but particularly toward the periphery, and the cones localized near the fovea.[111] The changes in the former, effected principally during vision in dim light, are not concerned with color sensation, as are the changes in cones which are brought about primarily by bright light.

The processes are regarded as deviations from photochemical stationary states set up during the period of accommodation to light of various intensities. Little is known as yet as to the photochemistry of materials in the cones.[112] The possibility that a flavin, known to occur in the retina, may be concerned with color vision and thus have to do in some manner with processes occurring in the cones has been mentioned by Theorell.[113]

Since the pioneering observations of Boll in 1877[114] it has been known that the rods contain a substance known as the visual purple, which is bleached by light. Weigert and Nakashima[115] investigated the photodichroism of the product as obtained from the retinas of frogs and spread in gelatin layers upon glass plates.

When applied to photographic plates, the visual purple usually diminishes rather than increases their sensitivity, but Kögel,[116] who reviewed the photochemical behavior of this material, observed a transient sensitization in a special case.

The bleaching of visual purple solutions in monochromatic light has been found to have a quantum efficiency of unity or very slightly less.[117]

The process is not one of oxidation, according to Brunner and Kleinau.[118] The oxidation-reduction potential curves of solutions of visual purple have been investigated by Pincussen, Suzuki and Seitz.[119] Kodama[120] has measured the glucolysis and oxygen consumption of the rat retina in light and in darkness. During the first thirty minutes, both the oxygen uptake and the aerobic glucolysis were much greater in darkness, but during the second thirty minutes the oxygen uptake diminished rapidly and approached the rate in light. The oxygen consumption was not proportional to the intensity of light with either continuous or short exposures. Aerobic glucolysis was but little influenced by the intensity of light. The gas exchange and oxygen consumption decreased temporarily in all cases in light, the latter showing the greater decrease. In colored light, the oxygen consumption was greatest in red, less in green and least in blue light. Aerobic glucolysis varied less, but in the same order. In sugar-free Ringer solution in darkness, the oxygen consumption was high at first but rapidly decreased to zero. The aerobic glucolysis was very low and quickly

[111] Hecht, S., *Physiol, Rev.*, **17,** 239 (1937); *J. Applied Phys.*, **9,** 156 (1938); Hartline, H. K., *Cold Spring Harbor Symposia Quant. Biol.*, **3,** 245 (1935).

[112] von Studnitz, G., *Arch. ges. Physiol. (Pflüger's)*, **239,** 515 (1937). Wald, G. [*Nature,* **140,** 545 (1937)] calls the violet cone pigment iodopsin. Vitamin A is probably related to it. Haig, C., Hecht, S. and Patek, A. J., Jr., *Science,* **87,** 534 (1938); Hecht, S. and Mandelbaum, J., *Ibid.*, **88,** 219 (1938).

[113] Theorell, H., *Biochem. Z.*, **279,** 186 (1935).

[114] Boll, F., *Arch. anat. Physiol.*, 4 (1877).

[115] Weigert, F., and Nakashima, M., *Naturwiss.*, **17,** 840 (1929).

[116] Kögel, G., *Phot. Korr.*, **65,** 138, 248 (1929); *Chem. Abs.*, **24,** 2068 (1930). Recent studies on the absorption spectrum of visual purple are due to Chase, A. M., and Haig, C., *J. Gen. Physiol.*, **21,** 411 (1938) and to Saito, Z., *Tohôku J. Exptl. Med.*, **32,** 432 (1938); *Chem. Abs.*, **32,** 9125 (1938).

[117] Dartnall, H. J. A., Goodeve, C. F., and Lythgoe, R. J., *Proc. Roy. Soc.*, **A156,** 158 (1936); **A164,** 216 (1938); Lythgoe, R. J., and Goodeve, C. F., *Trans. Ophthalmol. Soc.*, **57,** 88 (1937); Goodeve, C. F., *Sci. J. Roy. Coll. Sci.*, **8,** 9 (1938).

[118] Brunner, O., and Kleinau, W., *Monatsh.*, **68,** 244, 261 (1936).

[119] Pincussen, L., Suzuki, T., and Seitz, E. O., *Biochem. Z.*, **272,** 357 (1934).

[120] Kodama, S., *Tohôku J. Exptl. Med.*, **28,** 423 (1936); *Chem. Abs.*, **31,** 1081 (1937).

dropped to zero. In the presence of 0.1 per cent sugar in the Ringer solution in darkness, the oxygen consumption, high at first, rapidly decreased to one-fifth of its original value, but the aerobic glucolysis decreased but slightly. In the presence of 0.4 per cent of sugar, the oxygen uptake and aerobic glucolysis were comparatively low at the start and decreased but very little. In darkness, anaerobic glucolysis was equally high in solutions containing 0.1, 0.2 and 0.4 per cent of sugar. Jongbloed and Noyons,[121] also found the carbon dioxide production by frog retinas 22.5 per cent and the oxygen uptake 26.5 per cent greater in darkness than in white light.

Stutzke[122] observed that when the dark-adapted beef retina is exposed to light, ammonia is liberated, the ammonia content increasing from 200 to 500 per cent. This effect, which can be inhibited by glucose, lactate or pyruvate, is not observed in the light-adapted retina.

More recent studies of the behavior of the visual purple have revealed intimate relationships not only to such compounds as trimethylamine and creatinine, but also to carotenes, vitamin A, and the flavins.[123]

Observations on night blindness, a vitamin A deficiency,[124] led to the discovery of vitamin A in the normal retina. Wald[125] showed that mammalian retinas contain about 22 γ, and frog retinas 400 γ per gram of dry retina. The underlying pigment layers contain also xanthophyll. The function of the vitamin A is to serve as a precursor for the formation of the visual purple which is lost in the photochemical bleaching process. There is also present in the retina a faintly yellow pigment, known as retinene, of carotenoid nature. It does not occur free but associated with some other non-diffusible substance, probably a protein. In the light-adapted retina, the retinene is replaced by some vitamin A.

During vision the visual purple is converted photochemically into visual yellow which contains protein and retinene. This change is believed to be thermally reversible with regeneration of visual purple. Mirsky[126] suggests that the prosthetic group, retinene, is firmly bound in visual purple, and that the process of its bleaching to visual yellow consists in a denaturation of the protein after which the retinene is bound loosely if at all. He concludes the energy of activation of the denaturation to be low, the visual purple being denatured by a quantum of visible light. The function of the retinene in the visual purple may be to sensitize the protein denaturation to light.

When the visual yellow has been produced, it may either regenerate its precursor or lose some of its retinene which is then thermally converted into vitamin A and apparently lost to the retina by diffusion processes or in an unknown manner. This loss of visual purple has to be made up if night-blindness is to be averted, by a resynthesis by way of the underlying pigmented layer which Wald has shown to contain larger amounts of vitamin A. At least this is the case in the frog's eye, the retina of which has no blood supply.[127]

Details of the effects of temperature, pH and seasonal variations on the bleaching of visual purple have been reported by Chase,[128] who finds a photochemical decomposition product of certain retinal extracts to be an acid-base indicator, yellow in acid and colorless in alkaline solutions. He also states that the photodecomposition of the bile salt extracts of the retinas of summer frogs follows a first-order reaction course, but that of the extracts of winter frogs does not unless the extracts are made alkaline. The kinetics of the regeneration of bleached visual purple have recently been studied by Hecht, Chase, Schlaer and Haig.[129]

Some attention has been devoted to the nature and function of other pigments, such as the orange intermediate between visual purple and the products of its complete bleaching,[130] and also to a blue-sensitive substance, possibly a flavin, which Chase believes may, after its decomposition, be concerned in the regeneration of the visual purple.[131]

Porphyropsin, a purple pigment from the retina of fresh-water fish, also goes through a cycle in light, involving russet and yellow pigments.[132] Stern and Salomon,[133] suggest that the first step in the bleaching of visual purple may be a photodissociation of ovoverdin, rather than a denaturation of the protein carrier.

[121] Jongbloed, J., and Noyons, A., *Z. Biol.* **97,** 399 (1936); *Chem. Abs.,* **31,** 2691 (1937).

[122] Stutzke, S., *Klin. Wochschr.,* **15,** 524 (1936); *Chem. Abs.,* **30,** 6805 (1936).

[123] Brunner, O., *Oestern. Chem. Ztg.,* **40,** 203 (1937); Wald, G., and Zussman, H., *Nature,* **140,** 197 (1937).

[124] Blegvad, O., *Am. J. Ophthalmol,* **7,** 89 (1924); Fridericia, L. S., and Holm, E., *Am. J. Physiol.,* **73,** 63 (1925).

[125] Wald, G., *J. Gen. Physiol.,* **18,** 905 (1935); **19,** 781 (1936); *Nature,* **134,** 65 (1934).

[126] Mirsky, A. E., *Proc. Natl. Acad. Sci.,* **22,** 147 (1936). Krause, A. C., and Sidwell, A. E., Jr. *Am. J. Physiol.,* **121,** 215 (1938); *Arch. Ophthalmol.,* **18,** 807 (1937); suggest that the bleaching splits visual purple into protein and a colored lipid called visual yellow, which may be further bleached until colorless.

[127] See also Wald, G., and Clark, A.-B., *J. Gen. Physiol.,* **21,** 93 (1937).

[128] Chase, A. M., *J. Gen. Physiol.,* **19,** 577 (1936). See also Lythgoe, R. J., *J. Physiol.,* **89,** 331 (1937); Wald, G., *J. Gen. Physiol.,* **21,** 795 (1938).

[129] Hecht, S., Chase, A. M., Schlaer, S., and Haig, C., *Science,* **84,** 331 (1936). See also Hecht, S., Chase, A. M., and Shlaer, S., *Ibid.,* **85,** 567 (1937).

[130] Wald, G., *Nature,* **139,** 587 (1937).

[131] Chase, A. M., *Science,* **85,** 484 (1937).

[132] Wald, G., *Nature,* **139,** 1017 (1937).

[133] Stern, K. G., and Salomon, K., *Science,* **86,** 310 (1937).

Chapter 42

Photosensitized Biological Processes

The existence of a number of photosensitized reactions (discussed in Chapter 16) leads to the expectation that similar effects are to be encountered in biological processes. The first instance was reported by Raab from the laboratory of v. Tappeiner in 1899.[1] He observed that the dye acridine, in a dilution of 1:20,000, killed paramecia in six minutes in direct sunlight, in an hour in diffused light, and remained without effect for long periods in darkness. Many other dyes of widely different classes have similar effects, to which v. Tappeiner[2] applied the term "photodynamic actions."

Many recent workers have studied similar lethal effects on bacteria,[3] fungi[4] and various bacteriophages and viruses,[5] as well as the destructive effects upon their toxins.[6]

The hemolysis of red cells may be similarly sensitized,[7] notably by chlorophyll, which is effective even in dilutions of one in thirty million.[8] Hematoporphyrin, a product of the decomposition of hemoglobin, as well as other porphyrins, exhibits such properties in a marked degree.[9] When it is injected into mice no effects are produced until the animals are irradiated by sunlight or a carbon arc. Light causes itching, hyperemia of the ears, tail and snout, and, with sufficient doses of the sensitizer, the animals may die in light-stroke in a tetanic rigor. Desensitization occurs in darkness in about two weeks. The subject has been investigated to a considerable extent.[10]

[1] v. Tappeiner, H., *Z. Biol.*, **39**, 524 (1900).

[2] v. Tappeiner, H., *Deut. Arch. klin. Med.*, **80**, 427 (1904).

[3] Brocq-Rousseau, D., *Compt. rend. soc. biol.*, **119**, 272 (1935); *Chem. Abs.*, **29**, 5474 (1935); Szüts, A., *Magyar Orvosi Arch.*, **33**, 267 (1932); *Chem. Abs.*, **27**, 323 (1933); Vorster, D., *J. Dental Research*, **9**, 641 (1929); *Chem. Abs.*, **24**, 133 (1930); Philibert, A. and Risler, J., *Compt. rend.*, **183**, 1137 (1926); **186**, 1152 (1928); Ram, A., *Proc. Acad. Sci. United Provinces, Agra, Oudh, India*, **4**, 83 (1934); Boyet, D., *Helv. Chim. Acta*, **17**, 1460 (1934); T'ung,, T., and Zia, S. H., *Proc. Soc. Expt. Biol. Med.*, **36**, 326 (1937); Beck, L. V., and Nichols, A. C., *J. Cellular Comp. Physiol.*, **10**, 123 (1937); T'ung, T., *Proc. Soc. Exptl. Biol. Med.*, **38**, 29 (1938); Chin, T. L., *Ibid.*, **38**, 697 (1938).

[4] Gomez-Vega, P., *Arch. Dermatol. Syphilol.*, **32**, 49 (1935); *Chem. Abs.*, **30**, 572 (1936).

[5] Clifton, C. E., *Proc. Soc. Exptl. Biol. Med.*, **28**, 745 (1931); Linden, H., and Schwarz, F. K. T., *Arch. Hyg.*, **106**, 133 (1931); Prescher, W., *Planta (Abt. E., Z. wiss. Biol.)*, **17**, 461 (1932); *Chem. Abs.*, **27**, 3968 (1933); Perdrau, J. R., and Todd, C., *Proc. Roy. Soc.*, **112B**, 188, 277 (1933); Galloway, T. A., *Brit. J. Exp. Path.*, **15**, 97 (1934); Storey, H. H. *Ann. Applied Biol.*, **21**, 588 (1934); *Chem. Abs.*, **29**, 2203 (1935); Sheboldaeva, A. D., and Shugladze, A. K., *Z. Microbiol. Epidemiol. Immunitätsforsch. (U.S.S.R.)*, **18**, 466 (1937); *Chem. Abs.*, **32**, 7504 (1938).

[6] Lippert, K. M., *J. Immunol.*, **28**, 193 (1935); *Chem. Abs.*, **29**, 8048 (1935).

[7] Gachs, H., and Sacharoff, G., *Münch. Med. Wochschr.*, **52**, 297 (1905); Saeki, K., *Japan. J. Gastroenterol.*, **4**, 153, 166, 231, 244 (1932); *Chem. Abs.*, **27**, 1018 (1933); Angelica, V., *Boll. soc. ital. biol. sper.*, **8**, 1536 (1933); *Chem. Abs.*, **28**, 2767 (1934); Blum, H. F., Pace, N., and Garrett, R. L., *J. Cellular Comp. Physiol.*, **9**, 217 (1937).

[8] Hausmann, W., *Jahr. Wiss. Botanik*, **46**, 599 (1909).

[9] Kämmerer, H., and Weisbecker, H., *Arch. Exptl. Path. Pharmakol.*, **111**, 263 (1926); Squires, B. T., *Biochem. J.*, **21**, 437 (1927).

[10] Hausmann, W., and Löhner, L., *Biochem. Z.*, **173**, 7 (1926); Fabre, R., and Simonnet, H., *J. pharm. chim.*, **4**, 294 (1926); Supniewski, J. V., *J. Physiol.*, **64**, 30 (1927); *Chem. Abs.*, **22**, 455 (1928); Rock, E. N., and Howell, W. H., *Am. J. Physiol.*, **84**, 363 (1928); Smetana, H., *J. Exptl. Med.*, **47**, 593 (1928); Cuzin, J., *Bull. soc. chim. Biol.*, **12**, 1401 (1930); *Chem. Abs.*, **25**, 3368 (1931); Quin, J. I., *Rept. Director Vet. Services Onderstepoort*, **17**, Pt. 2, 645 (1931); *Chem. Abs.*, **27**, 5421 (1933); Szörenyi, E. T., *Biochem. Z.*, **252**, 113 (1932); *Boll. soc. ital. biol. sper.*, **7**, 835, 866 (1932); Robuschi, L., *Biochem. terap. sper.*, **23**, 54 (1936); *Chem. Abs.*, **30**, 5245 (1936); Hausmann,

Meyer-Betz[11] took 0.2 gram of hematoporphyrin intravenously. Irradiation by a carbon arc led to the production of a lesion which had some resemblance to those of hydroa. The immediate reaction was merely reddening and edema, but on the following day the area was infiltrated, reddened and painful, and rendered almost black by multiple hemorrhages. After a week, there was superficial necrosis, followed by the formation of a thick black scab. The sun produced on exposed areas a very severe dermatitis which began immediately after the exposure and progressed for several days. It was marked by extreme pain, swelling and induration, and was followed by a heavy pigmentation. Two cases of chronic porphyrinuria have recently been reported in which the face and hands were highly pigmented, although not hypersensitive to ultraviolet light.[12]

A disease in which there is marked sensitivity to light is the rare and usually fatal xeroderma pigmentosum or Kaposi's disease.

In human pathology, true light urticarias are rare.[13] It has been suggested that hydroa vacciniforme represents a slight sensitization due to hematoporphyrin or other porphyrins produced by solar ultraviolet light from some precursor which was assumed to be present in the skin. The basis for this theory of the origin of the disease is the frequent association of a porphyrinuria. It may, however, be noted that porphyrinuria may occur from certain causes without causing light sensitivity.[14]

Certain diseases of animals have been attributed to photosensitization. After eating buckwheat, and especially the green parts of the plant, oxen, swine and sheep, on exposure to light, become greatly excited and dance about wildly because of the sensory stimulation of rapidly developing skin lesions. This disease, known to Hertwig as early as 1833, has been studied by Sheard, Caylor and Schlotthauer,[15] who suggest that the sensitizer may be phylloporphyrin or possibly cholehematin.

The weed, St. John's wort, Hypericum, brings about similar symptoms in range animals, and it has been stated that Arabs used to stain their white horses with tobacco or henna to protect them from light in regions where this weed abounds. Ionnides[16] isolated a pigment from the plant which photosensitized white rats, but its constitution is unknown.

A disease of sheep and Angora goats, Geelgikop, characterized by the sudden onset of a swelling of exposed parts of the head and ears,[17] is caused by eating *Tribulus terrestris*.

W., and Kuen, F. M., *Biochem. Z.*, **265**, 105 (1933); Guerrini, G., *Boll. soc. ital. biol. sper.*, **6**, 401 (1931); *Chem. Abs.*, **26**, 772 (1932). Other substances may act, as trypaflavine, John, H., [*Biochem, Z.*, **155**, 159 (1925)], bacterial extracts, Risler, J., and Philibert, A., [*Compt. rend. soc. biol.*, **96**, 747 (1927); *Chem. Abs.*, **21**, 1844 (1927)], and bile, Condorelli, F., *Arch. fisiol.*, **28**, (1930); *Chem. Abs.*, **25**, 3711 (1931).

[11] Meyer-Betz, F., *Deut. Arch. Klin. Med.*, **122**, 476 (1913).

[12] Roth, E., *Deut. Arch. Klin. Med.*, **178**, 185 (1935). For congenital porphyrinuria in cattle, Rimington, C., *Onderstepoort J. Vet. Sci. Animal Ind.*, **7**, 567 (1936); *Nature*, **140**, 105 (1937); *Chem. Abs.*, **31**, 7108 (1937); Fröhlich, W., *Wien. Klin. Wochschr.*, **51**, 791 (1938); *Chem. Abs.*, **32**, 8510 (1938).

[13] The relation of sensitization to light to dermatology has been reviewed by Eidinow, A., *Proc. Roy. Soc. Med.*, **28**, 633 (1935); Mathews, F. P., *Arch. Path.*, **23**, 399 (1937); *Chem. Abs.*, **31**, 5430 (1937). See also Ambroglio, A., *Arch ital. dermatol. sifilog. venereol.*, **13**, 546 (1937); *Chem. Abs.*, **32**, 2216 (1938); Urbach, F., *Klin. Wochschr.*, **17**, 304 (1938); *Chem. Abs.*, **32**, 7116 (1938).

[14] Hausmann, W., and Kuen, F. M., *Biochem. terap. sper.*, **21**, 441 (1934); *Chem. Abs.*, **29**, 1875 (1935).

[15] Sheard, C., Caylor, H. P., and Schlotthauer, C. P., *J. Exptl. Med.*, **47**, 1013 (1928).

[16] Ionnides, Z. M., *Arch. Inst. Pasteur Hellen.*, **2**, 161 (1928); *Chem. Abs.*, **25**, 1869 (1931); *Compt. rend soc. biol.*, **105**, 349 (1930); *Chem. Abs.*, **25**, 1869 (1931).

[17] Quin, J. I., and Rimington, C., *South African J. Sci.*, **30**, 461 (1933); *Chem. Abs.*, **28**, 2056 (1934); Quin, J. *Onderstepoort J. Vet. Sci.*, **1**, 459, 469, 497, 501, 505 (1933); **3**, 137 (1934); **4**, 463; *Chem. Abs.*, **28**, 2790 (1934); **29**, 7351 (1935); Rimington, C., Quin, J. I., and Roets, G. C. S., *Onderstepoort J. Vet. Sci. Animal Ind.*, **9**, 225 (1937); *Chem. Abs.*, **32**, 4660 (1938).

A wide variety of other physiological and pathological effects due to the action of light and sensitizers has been enumerated by Blum.[18] Among others mentioned are the inhibition of clotting of the blood by fibrinogen in the presence of light and methylene blue, stimulation of nerves, contraction of isolated skeletal muscles bathed by the photosensitizer solution, and production of arythmias in the isolated turtle or mammalian heart perfused with photosensitizing solutions and exposed to light.

The hydrolysis of serum albumin may be effected by hematoporphyrin and oxygen in light.[19] The porphyrin unites with the protein, becomes excited by the absorption of light, combines with oxygen and passes a part of its energy over to the protein molecule.

A number of generalizations have been made by Blum regarding these processes.[20] Although most sensitizers are fluorescent, the fluorescent rays they emit are not responsible for the effects produced and there is no quantitative relation between the fluorescence of a sensitizer and its biological effectiveness. The substances absorb chiefly in the visible range, and only the absorbed energy is effective biologically. (The possibility of sensitization to ultraviolet rays cannot be excluded.) Most of the effects produced by these substances in light can also be produced by them, although much more slowly, in darkness. The presence of oxygen appears to be essential for the processes occurring in light.[21] Most effects in this category can be inhibited by blood serum and particularly by its albumin. Because of this action, the injection of dyes which hemolyze red blood cells *in vitro* is not followed by hemolysis in animals subsequently exposed to light.

Sensitization to various ultraviolet radiations may be effected by certain substances, such as acridine or trypaflavine, which make the region in the vicinity of 3650A active.[22] Ethyl chlorophyllide sensitizes especially to 3130 or 3650A, as well as to visible rays. Carotene sensitizes to the range of 2800 to 4350A, but in the shorter ultraviolet or visible rays is less effective than chlorophyll.[23]

Attempts to utilize photodynamic substances in therapy have not proved encouraging. Kreidl and Nozicka [24] suggest that the therapeutic action of light may be promoted by injecting anthracene, anthraquinone or their derivatives. Eosin was at one time believed to cause a rapid loosening of necrotic tissues in luetic or tuberculous ulcers on exposure to sunlight. In connection with such attempts, it may be noted that urticarial reactions are readily produced. The intradermal injection of two drops of a 1:1000 solution of eosin renders the skin so sensitive that a few minutes of exposure to light produces an urticarial wheal.

An understanding of the mechanism of photosensitized biological processes is of importance because of the light it may cast upon the nature of the function of chlorophyll in the photosynthesis of carbohydrates. Noack [25] early divided photosensitizers into two classes: certain heavy metal salts and fluorescent organic dyes. Both serve as carriers of oxygen, the former by a change in valence of the metal

[18] Blum, H. F., *Physiol. Rev.*, **12**, 23 (1932); Sellards, S. W., *J. Med. Research*, **38**, 293 (1918); Dognon, A., *Compt. rend. soc. biol.*, **98**, 283 (1928).

[19] Boyd, M. J., *J. Biol. Chem.*, **103**, 249 (1933).

[20] See also Blum, H. F., *Biol. Bull.*, **59**, 81 (1930); *Chem. Abs.*, **26**, 4645 (1932).

[21] Blum, H. F., and McBride, G. C., *Biol. Bull.*, **61**, 316 (1931); *Chem. Abs.*, **26**, 2523 (1932); Blum, H. F., *J. Cellular Comp. Physiol.*, **9**, 229 (1937); Spealman, C. R., and Blum, H. F., *Univ. Calif Pub. Physiol.*, **8**, 147 (1937).

[22] Kuen, F. M., and Rosenfeld, P., *Biochem. Z.*, **254**, 181 (1932).

[23] Kuen, F. M., and Püringer, K., *Biochem. Z.*, **286**, 196 (1936).

[24] Kreidl, I., and Nozicka, F., Austrian Patent, 142,163, June 25, 1935; *Chem. Abs.*, **29**, 6365 (1935). The claims that hematoporphyrin can enable visible light to cure rickets are doubtless in error in view of the work of Windaus on sensitized reactions of ergosterol. (Chapter 39.) Rezzesi, F. D., *Biochem. terap. sper.*, **24**, 274 (1937); *Chem. Abs.*, **32**, 650 (1938). Tests by Marique, P. [*Bull soc. chim. biol.*, **20**, 325 (1938); *Chem. Abs.*, **32**, 5039 (1938)] gave negative results.

[25] Noack, K., *Z. Botan.*, **12**, 273 (1920); *Chem. Abs.*, **15**, 2453 (1921).

and the latter by a formation of peroxides. The action of the latter substances can be stopped by such reducing agents as sodium sulfite. Gaffron [26] found that solutions of hematoporphyrin, chlorophyll or dyes in serums at pH 11.4 absorb oxygen on exposure to light with the oxidation of the protein to which the dyes become attached. Carbon dioxide and ammonia are liberated. The greater part of the former is ascribed to the action of acids liberated during oxidation upon the serum. Tyrosine, phenol and uric acid in alkaline solution can also be oxidized in this manner by dyes, such as eosin, erythrosin or Rose bengal. Aliphatic substrates are not so oxidized, according to Carter.[27] The introduction of an hydroxy or an amino-group renders benzene derivatives susceptible to this type of reaction. Side-chains in which the groups NH_2 and CH=CH occur were oxidized, as were ring compounds, such as α-naphthol, tryptophane, tyrosine, thiophene and purine derivatives. Carter did not believe that hydrogen peroxide is formed in the process, which was neither accelerated by iron salts nor retarded by potassium cyanide.[28] Some have found such processes to be increased by cyanide.[29] Wohlgemuth and Szörényi believe that true tissue respiration is lowered from 2 to 18 per cent by visible or ultraviolet light. Sensitizers in darkness also reduce it. Illumination of tissue sections in the presence of hematoporphyrin or Rose bengal increases oxidation and this action is stimulated by cyanides. The true respiration, which they regard as distinct from this photoöxidation, is believed to be reduced from 17 to 43 per cent. Sensitizers also decrease the usual stimulating effect of light on anaerobic glycolysis. In red cells, sensitizers produce methemoglobin especially when illuminated.[30] Hematoporphyrin increases the absorption of oxygen by red blood cells, especially in light, but there is no corresponding production of carbon dioxide. Photographic desensitizers as Pinakryptol green retard this.[31] Attempts to isolate peroxides of fluorescent dyes which promote the transportation of oxygen in analogy with the assumed chlorophyll peroxide of Willstätter were unsuccessful, according to Gaffron.[32] Acceptor peroxides were, however, produced during the photoöxidation of aliphatic amines in the presence of chlorophyll. When a solution of chlorophyll in amylamine was exposed to light and then placed in darkness, the quantity of peroxidic oxygen was approximately equal to the amount of molecular oxygen absorbed. This oxygen was quantitatively evolved when a catalyst, such as manganese dioxide was added to the darkened solution. The photochemical action depended greatly upon the solvent chosen, increasing more than a hundred times when acetone or pyridine replaced water. The absorption of oxygen ultimately reached two molecules for each molecule of primary or secondary amine. Gaffron [33] dissolved ethyl chlorophyllid and allylthiourea in acetone and exposed the solution to monochromatic light in the presence of oxygen. The relation between the energy absorbed and the oxygen consumed was in agreement with the Einstein law, provided that the concentration of the acceptor was at least 7.5×10^{-1} moles per liter, or when the acceptor concentration was over 100 times that of the dye. Similar results were reported with hematoporphyrin as the dye.

[26] Gaffron, H., *Naturwiss.*, **13**, 859 (1925); *Biochem. Z.*, **179**, 157 (1926).

[27] Carter, C. W., *Biochem J.*, **22**, 575 (1928).

[28] See also Blum, H. F., and McBride, G. C., *Biol. Bull.*, **61**, 316 (1931); *Chem. Abs.*, **26**, 2523 (1932).

[29] Bier, O. G., and Roche e Silva, M., *Compt. rend. soc. biol.*, **118**, 911, 914 (1935); *Chem. Abs.*, **29**, 3727 (1935); Wohlgemuth, J., and Szörényi, E., *Biochem. Z.*, **264**, 371, 389, 406 (1933).

[30] See also Chocetta, A., *Boll. soc. ital. biol. sper.*, **7**, 1545 (1932); *Chem. Abs.*, **27**, 2731 (1933).

[31] Szörényi, E., *Biochem. Z.*, **252**, 113 (1932). See also Smetana, H., [*J. Biol. Chem.*, **124**, 667, 741, 745 (1938)] who finds the proteins of blood and the uric acid of urine the acceptors.

[32] Gaffron, H., *Ber.*, **60B**, 2229 (1927).

[33] Gaffron, H., *Ber.*, **60B**, 755 (1927).

Blum and Spealman[34] believed the peroxide formed when fluorescent dyes alone are irradiated in aqueous solutions to be hydrogen peroxide formed from water and oxygen. They suggest that the bleaching of excited dye molecules may be due to their oxidation by the hydrogen peroxide.

There has been much discussion as to whether, in the dye-sensitized oxidations of various substances, it is the oxygen itself or the oxygen acceptor which receives the energy of the light-excited dye. Gaffron[35] does not believe the former can account for the facts. Even in cases in which it is the sensitizer itself which is oxidized, Gaffron believes that there are other molecules of the sensitizer which receive enough energy from the light-excited molecules to convert them into a long-lived form capable of being oxidized. Data on the quantum yields in the oxidation of rubrene were advanced in support of this view, but have recently been the subject of some discussion. (See Chapter 26.)

On the other hand, Kautsky and Hirsch,[36] in work on the oxidation of isoamylamine in the presence of chlorophyll, assumed that oxygen was activated by the transfer of energy from a metastable intermediary state of the pigment. The energy required for the activation of oxygen was calculated to be 37 kcal. (7620A). Energy of longer wave-lengths should not be able, therefore, to cause the reaction. To test this, Gaffron[37] filtered out practically all light of wave-length shorter than 7600A by the use of 6 mm. of B G 3, Schott glass. Bacterial pheophytin was used, since chlorophyll does not absorb in this range; thiosinamine was the acceptor. Since photoöxidation still occurred, it seems that activation of oxygen is not the mechanism, and it must be the acceptor molecules which receive the energy of the excited dye. When organic substrates are oxidized in the presence of chlorophyll, one molecule of oxygen is used for each quantum of light absorbed regardless of the wave-length, except at wave-lengths where the quantum is too small and the reaction does not proceed. Further evidence that it is the oxygen-acceptor which acquires the energy has been given by Franck and Levi.[38] They suggest that the chlorophyll on absorption may form hydrogen and free radicals instead of forming a metastable excited molecule. These may subsequently reunite, with the production of a chemiluminescent glow. In the presence of oxygen, the hydrogen is oxidized. The acceptor takes over the energy absorbed by the chlorophyll. This offered a possible explanation of the fact that the fluorescence, which represents but a small part of the energy, is slightly extinguished by oxygen. The problem is still in a somewhat speculative state. Because of its relation to other photosensitized processes by which carbon dioxide and water are synthesized to carbohydrates in the green plant, the mechanism of these reactions is being actively investigated.

By continuously irradiating a dilute solution of sodium fluorescein, Menke[39] made a photofluorescein. It was separated by filtering after precipitation with a small amount of hydrochloric acid. After washing with water, the precipitated dye was dissolved in alkali and the sodium salt crystallized by careful evaporation. This material was then dissolved in Locke's solution so that each cc. contained a mg. of photofluorescein. It then hemolyzed rat blood in darkness to the same extent

[34] Blum, H. F., and Spealman, C. R., *J. Phys. Chem.*, **37,** 1123 (1933).

[35] Gaffron, H., *Biochem. Z.*, **264,** 251 (1933).

[36] Kautsky, H., and Hirsch, A., *Ber.* **64,** 2677 (1931); Kautsky, H., de Bruijn, H., Neuwirth, R., and Baumeister, W., *Ber.*, **66,** 1598 (1933); Kautsky, H., and Hirsch, A., *Biochem. Z.*, **278,** 374 (1935); Kautsky, H., Hirsch, A., and Flesch, W., *Ber.*, **68,** 152 (1935).

[37] Gaffron, H., *Ber.*, **68B,** 1409 (1935); *Chem. Abs.*, **29,** 8056 (1935) .

[38] Franck, J., and Levi, H., *Naturwiss.*, **23,** 229 (1935).

[39] Menke, J. F., *Biol. Bull.*, **68,** 360 (1935); *Chem. Abs.*, **29,** 5871 (1935).

that fluorescein does in light, although the non-irradiated fluorescein had no apparent action in darkness. Approximately two hours in darkness were required for a 1:2000 dilution of the photofluorescein to hemolyze one cc. of 1 per cent red blood cells. Blum[40] believes that eosin dyes in dilute solutions show hemolysis of red blood cells in darkness only in the presence of hydrogen peroxide.

This résumé is necessarily too brief to give an adequate impression of the great number of investigations in this field which are of importance to the zoölogist or botanist rather than to the photochemist.[41]

That eosin and hematoporphyrin, when applied to the skin of mice and exposed for three months to sunlight, may produce skin tumors, has been noted by Büngeler.[42] Certain carcinogenic agents, such as benzopyrene, shale oil and coal tar, exhibit a photodynamic action on paramecia.[43]

[40] Blum, H. F., *Cold Spring Harbor Symposia Quant. Biol.*, **3,** 318 (1935).

[41] See, for further details: Kosman, A. J., and Lillie, R. S., *J. Cellular Comp. Physiol.*, **6,** 505 (1935); *Chem. Abs.*, **29,** 8098 (1935); Hinrichs, M., *Biol. Bull.*, **50,** 1 (1926); Guerrini, G., *Boll. soc. ital. biol. sper.*, **8,** 1357 (1933); *Chem. Abs.*, **28,** 1726 (1934); Macht, D. I., *Proc. Soc. Exptl. Biol. Med.*, **23,** 638, 639 (1926); Sunzeri, G., *Arch. fisiol.*, **33,** 555 (1934); *Chem. Abs.*, **29,** 1883 (1935); Welsh, J. H., *Biol. Bull.*, **66,** 346 (1934); *Chem. Abs.*, **28,** 346 (1934); Efimov, A., and Efimov, W. W., *Biochem Z.*, **155,** 376 (1925); Schanz, F., *Ber. botan. Ges.*, **41,** 165 (1923); *Chem. Abs.*, **17,** 3040 (1923); Blum, H. F., and Scott, K. G., *Plant Physiol.*, **8,** 525 (1933); Jirovec, O., and Ziegler, Z., *Z. ges. Exptl. Med.*, **90,** 651 (1933); *Chem. Abs.*, **29,** 4031 (1935); Zikes, H., *Centr. Bakt. Parasitenk.*, **II, 65,** 128 (1925); *Chem. Abs.*, **20,** 1423 (1926); Teplov, I. and Dobrokhotova, E., *Arch. sci. biol. U.S.S.R.*, **32,** 72 (1932); *Chem. Abs.*, **27,** 3492 (1933); Macht, D. I., and Teagarden, E. J., Jr., *J. Pharmacol.*, **22,** 21 (1923); Roskin, G., and Romanova, K., *Z. Immunitäts,* **72,** 445 (1931); *Chem. Abs.*, **26,** 2790 (1932); Azzi, A., *Arch. Sci. Med.*, **45,** 212 (1922); *Chem. Abs.*, **17,** 3541 (1923); Monasterio, G., *Arch. Farmacol. Sper.*, **51,** 111 (1930); *Chem. Abs.*, **25,** 2486 (1931); Spealman, C. R., and Blum, H. F., *J. Cellular Comp. Physiol.*, **3,** 397 (1933); *Chem. Abs.*, **28,** 3089 (1934); Hinrichs, M. A., and Kosman, A. J., *J. Cellular Comp. Physiol.*, **6,** 487 (1935); Lippay, F., *Klin. Wochschr.*, **6,** 651 (1927); *Chem. Abs.*, **21,** 2706 (1927); Nitta, B., *Folia Pharmacol. Japon.*, **17,** 72 (1928); *Chem. Abs.*, **32,** 3434 (1938); Kosman, A. J., *J. Cellular Comp. Physiol.*, **11,** 279 (1938); *Chem. Abs.*, **32,** 6677 (1938); Zia, S. H., Chow, B. F., and T'ung, T., *Proc. Soc. Exptl. Biol. Med.*, **38,** 688 (1938).

[42] Büngeler, W., *Z. Krebsforsch.*, **46,** 130 (1937); *Chem. Abs.*, **31,** 8670 (1937).

[43] Mottram, J. C., and Doniach, I., *Nature,* **140,** 933 (1937); *Lancet,* **I,** 1156 (1938).

Chapter 43

Photosynthesis of Carbohydrates[1]

With the help of sunlight, the green plant builds up from carbon dioxide, water and salts the sugars and starches which serve as the foodstuffs of man. At the same time, oxygen is liberated. The photosynthetic process may be represented by the equation:

$$CO_2 + H_2O + \text{light} \rightarrow CH_2O + O_2.$$

The hypothetical formaldehyde is assumed to be subsequently converted into sugars and starches. The energy required for this endothermic reaction must be supplied as light. This is absorbed by chlorophyll, the green pigment of the leaves, which in some as yet unknown manner acts as a photosensitizer for the reaction. The energy required for the synthesis of formaldehyde is at least 134 kcal., and possibly more.[2] Since the effective wave-lengths in the visible range may be as long as about 7000A, corresponding to only about 40 kcal., it is apparent that the absorption of one quantum per molecule would not provide sufficient energy to supply that needed for the reaction. It is essential, therefore, that at least three and more likely four quanta be absorbed for each molecule of carbon dioxide assimilated or of oxygen liberated. The nature of the coupled series of reactions underlying the photosynthetic process is not as yet understood, although ever-increasing attention has been devoted to the problem.

The investigations in this field may be divided into those concerned with the photochemical mechanism involved, as it might possibly be conceived of as occurring *in vitro* (in the presence of the extracted sensitizing pigment) and into those which actually occur in the plant. The latter studies belong in the realm of the plant physiologist and involve many complicated features, such as the influences of the stomatal openings within the leaf by which the gases gain entrance and egress, the nature and orientation of the chloroplasts (the histological regions within which the chlorophyll occurs), the amounts of energy reflected, absorbed and transmitted by the leaf, etc. For a discussion of these factors special works must be consulted.[3] It is possible here to mention merely some calculations of the efficiency of the process as it occurs in an acre of corn, which have been made by Transeau.[4] Assuming a yield of 100 bushels per acre, 10,000 corn plants on an acre yield a dry weight of 2160 kg. of corn. The total dry weights of the plants at maturity would be about 6000 kg. After deducting 322 kg. of mineral matter there would be a residue of 5678 kg. of organic matter, of which about 2675 kg. is carbon. The glucose equivalent of this is 6678 kg. This is less than the true amount formed, since some would have been consumed in

[1] A recent review is given by W. M. Manning, *J. Phys. Chem.*, **42**, 815 (1938).

[2] Blum, H. F., *Am. Naturalist*, **71**, 350 (1937).

[3] Stiles, W., "Photosynthesis, The Assimilation of Carbon by Green Plants," London, Longmans, Green, 1925; Spoehr, H. A., "Photosynthesis," New York, The Chemical Catalog Co., Inc. (Reinhold Publishing Corp.), 1926; Stiles, W., *Sci. Progress*, **25**, 590 (1931); Baly, E. C. C., *Sci. J. Roy. Col. Sci.*, **2**, 58 (1932).

[4] Transeau, E. N., *Ohio J. Sci.*, **26**, 1 (1926).

respiration during the life of the plants. This is estimated at 2045 kg. so that the total glucose made by the plants would have been 8732 kg. This is estimated to have required not far from 33 million calories of energy. The total energy of sunlight falling during this period on the acre is estimated as 2043 million calories, so that about 1.6 per cent of the light energy might have been used in photosynthesis. If it be assumed that only about 20 per cent of the incident radiant energy is in the wave-length regions capable of causing photosynthesis, then the overall efficiency of this light would be raised to about 8 per cent. There are several reasons for this low value. There are large reflection losses and some energy is lost by transmission.[5] During a large part of the growing period, much of the energy reaches merely the ground instead of the leaves of the plants, causing a loss estimated for the period at about 54 per cent. Respiration liberates about a quarter of the energy absorbed in the photosynthetic process. Another loss is in the energy required for transpiration. For every kilogram gained in dry weight, about 276 are evaporated during the growing season.

Formaldehyde as Intermediate. Von Baeyer[6] seems to have been the first to suggest the formation of formaldehyde in an initial stage of the process. Sabalichschka[7] showed that certain plants, when deprived of carbon dioxide and supplied with formaldehyde, polymerize the latter to sugars and starch, even in the absence of light. From a study of the assimilatory quotient CO_2/O_2, Willstätter and Stoll[8] contend that formaldehyde is the only intermediate possible between carbon dioxide and the carbohydrates. This quotient under all conditions was found experimentally to be one, that indicated by the equation in the first paragraph. For the formation of glycollic acid, it would be 1.33, for formic acid 2.0 and for oxalic acid 4.0. That formaldehyde under the influence of ultraviolet light of wave-lengths scarcely transmitted by glass acquires the power of reducing copper sulfate in the presence of sodium citrate or carbonate was claimed by Moore and Webster.[9] This assumed photocondensation of formaldehyde (see Chapter 22) did not require the presence of an inorganic activator, probably proceeded at its maximum velocity when the concentration of formaldehyde was approximately 5 per cent and was aided by a slight alkalinity. Ram and Dhar[10] claim to have obtained small yields of reducing sugars when aqueous formaldehyde was exposed to sunlight in the presence of ferric chloride or kieselguhr. In the mixture of sugars (formose) which results from the polymerizing action of certain alkaline condensing agents on formaldehyde, Küster and Schoder[11] have identified *dl*-fructose, a ketopentose and sorbose. Ascorbic acid has been said by West and Ney[12] to be an active catalyst for the formation of reducing sugars from formaldehyde. It is unlikely that a photocondensation of formaldehyde of the type studied in *in vitro* experiments plays a significant role in the processes by which the plant forms sugars and cellulose.

Klein and Werner[13] claim to have detected the production of formaldehyde as an intermediate in assimilation. Other aldehydes have, however, occasionally

[5] Shull, C. A., *Science*, **67**, 107 (1928).

[6] von Baeyer, A., *Ber.*, **3**, 68 (1870).

[7] Sabalichschka, T., *Z. Angew. Chem.*, **5**, 684 (1922); *J. Soc. Chem. Ind.*, **42**, 65A (1923).

[8] Willstätter, R., and Stoll, A., *Ber.*, **50**, 1777 (1917).

[9] Moore, B., and Webster, T. A., *Proc. Roy. Soc.*, **90**, 168 (1918); *Chem. Abs.*, **12**, 1992 (1918).

[10] Ram, A., and Dhar, N. R., *J. Indian Chem. Soc.*, **14**, 151 (1937); *Chem. Abs.*, **31**, 7455 (1937).

[11] Küster, W., and Schoder, F., *Z. physiol. Chem.*, **141**, 110 (1924).

[12] West, E. S., and Ney, L. F., *Science*, **84**, 294 (1936).

[13] Klein, G., and Werner, O., *Biochem. Z.*, **68**, 361 (1926).

been suggested as intermediary products in natural photosynthesis.[14] Acetaldehyde has been discussed as such by Klein and Pirschle.[15] Some, like Barton-Wright and Pratt[16] believe the first sugar formed to be a hexose. Parkin,[17] however, believes that the bulk of the hexose sugars detectable in the leaf arise as a result of the inversion of sucrose. Bodnár, Róth and Bernauer[18] believe that, although in the leaves of *Tropaeolum majus,* formaldehyde gives rise to sugars, its presence inhibits the condensation of sugars to starch.

Attempts to Obtain Photosynthesis Without Chlorophyll. One attack has involved the use of ultraviolet light in the effort to duplicate *in vitro* some of the processes of photosynthesis. Since these attempts have avoided the use of the plant pigments and have employed ultraviolet light of wave-lengths far shorter than those available in sunlight, it is evident that the results can tell but little regarding the occurrences which actually take place in the plant under physiological conditions. If these attempts are viewed in the light of experiments conducted to determine the possibility of artificially producing the carbohydrates as food materials independently of the plant, they afford little hope for a practical outcome. The energy required to produce the carbohydrates which have been claimed in even the most promising of these experiments is far greater than the energy bound in the carbohydrate reaction products.

Baly and Heilbron[19] claimed that detectable quantities of formaldehyde result when an aqueous solution of carbon dioxide is exposed to ultraviolet rays with agitation. The agitation was thought to decrease the local formation of hydrogen peroxide which prevented the possibility of obtaining a formaldehyde test by oxidizing that material to formic acid. In these early experiments it was believed that evidence had been advanced that wave-lengths less than 2200A might produce one or two parts of formaldehyde in 100,000 of carbon dioxide solution in 18 to 72 hours. If wave-lengths of about 2900A were simultaneously used, it was believed that the formaldehyde was polymerized to reducing sugars.

Similar claims had been made previously, although in these, other substances had been employed as catalysts. Moore and Webster[20] claimed to have detected formaldehyde when carbon dioxide solutions containing colloidal uranium oxide were exposed to sunlight, thus confirming still earlier observations of Bach[21] and of Usher and Priestley.[22] Baly and coworkers also claimed to have obtained positive results in visible light by the use of a number of the catalysts of Moore and others, although they were at one time of the opinion that these may have acted instead as internal filters capable of removing those ultraviolet rays which polymerize formaldehyde. Thus this substance might be allowed to accumulate in quantities sufficient for detection. Malachite green, methyl orange, as well as colloidal uranium compounds and ferric hydroxide were, however, believed true catalysts. Baly also emphasized the necessity of controlling the hydrogen ion concentration of the irradiated solutions by maintaining an excess of magnesium carbonate.

[14] Griebel, C., *Z. Unters. Nahr. Genussm.,* **48,** 218 (1924).

[15] Klein, G., and Pirschle, K., *Biochem. Z.,* **158,** 340 (1926).

[16] Barton-Wright, E. C., and Pratt, M. C., *Biochem. J.,* **24,** 1210, 1217 (1930); see also Klason, P., *Svensk Kem. Tids.,* **46,** 208 (1934); *Chem. Abs.,* **29,** 2576 (1935); Gordon, R. B., *Ohio J. Sci.,* **29,** 131 (1929); *Chem. Abs.,* **23,** 3951 (1929); Priestley, J. H., *New Phytol.,* **23,** 255 (1924); *Chem. Abs.,* **19,** 3291 (1925).

[17] Parkin, J., *New Phytol.,* **24,** 57 (1925); *Chem. Abs.,* **20,** 3022 (1926).

[18] Bodnár, J., Róth, L. E., and Bernauer, C., *Biochem. Z.,* **190,** 305 (1927); see also Kretovich, V., *Z. physiol. Chem.,* **231,** 265 (1935).

[19] Baly, E. C. C., and Heilbron, I. M., *J. Soc. Chem. Ind.,* **40,** 377 (1921); Baly, E. C. C., Heilbron, I. M., and Barker, W. F., *J. Chem Soc.,* **119,** 1025 (1921); *Nature,* **112,** 323 (1923); Baly, E. C. C., *Ind. Eng. Chem.,* **16,** 1018 (1924).

[20] Moore, B., and Webster, T. A., *Proc. Roy. Soc.,* **B87,** 168 (1913); **B90,** 168 (1918); *Chem. Abs.,* **12,** 1992 (1918).

[21] Bach, A., *Compt. rend.,* **116,** 1145 (1893).

[22] Usher, F. L., and Priestley, J. H., *Proc. Roy. Soc.,* **77B,** 369 (1906); **78B,** 322 (1906); Ferrous salts were believed effective by Stoklasa, J., and Zdobnicky, W., *Ber.,* **50,** 1777 (1917); *Centr. Biochem. Biophys.,* **18,** 370.

Many chemists attempted without success to confirm these observations.[23]

During this period, Baly[24] claimed also to have synthesized large amounts of reducing sugars by exposing aqueous 40-per cent formaldehyde solutions to the rays of the quartz mercury arc in the presence of calcium carbonate. By certain concentration methods, there was obtained a viscous syrup with sweet taste and reducing properties. An examination of this material by Irvine and Francis[25] showed no ketoses, polysaccharides or anhydro-sugars, but about 9.3 per cent of sugars and 80 per cent of non-sugar compounds containing hydroxyl groups.

In subsequent work, Baly, Davies, Johnson and Shanassy[26] concluded that the substance first formed from carbon dioxide might be some complex aldehyde other than formaldehyde. They also claimed that complex organic compounds may be synthesized by the action of ultraviolet light on suspensions of various insoluble powders, such as aluminum, barium sulfate, aluminum hydroxide, and basic carbonates of aluminum, magnesium and zinc, in water through which a stream of carbon dioxide is passed. It was thought essential that the carbon dioxide be adsorbed on these materials. The compounds produced appeared to be of the nature of complex carbohydrates. It was also believed[27] that the total amount of material photosynthesized at a colored surface by visible light was greater than that produced at a white surface by ultraviolet light. Nickel or cobalt carbonates were thought particularly effective, although easily poisoned.

Baur and Rebmann,[28] in a repetition of the Moore and Webster experiments were unable to detect formaldehyde, oxalic or glyoxalic acids. Baur and Büchi[29] attributed the formation of carbohydrates in experiments with dyestuffs such as malachite green to a decomposition of the dye rather than to true photosynthesis from carbon dioxide. Their observations were in general confirmed by Dean Burk,[30] who employed condensed sunlight. Nevertheless, the amounts of formaldehyde produced from the dye itself were very small. Amines are also produced, and under aerobic and alkaline conditions, nitrites as well.

Emerson[31] was unable to obtain any photosynthetic effects by the use of a purified nickel carbonate preparation.

Recently, Dhar and Ram[32] claimed that from 100 cc. of a 10-per cent solution of potassium carbonate mixed with one gram of powdered magnesium and in the presence of zinc oxide, gave after 5.5 hours of exposure to direct sunlight 0.0045 gram of formaldehyde, although no reducing sugar could be detected.[33] The occurrence of traces of formaldehyde in rain water was attributed to the action of light of wave-length 2550A, which had escaped absorption by the ozone layer. Decomposition of formaldehyde by the wave-length 2660A is thought to be hindered by the presence of hydrogen in the upper atmosphere.

[23] Spoehr, H. A., *J. Am. Chem. Soc.,* **45,** 1185 (1923); Porter, C. W., and Ramsperger, H. C., *J. Am. Chem. Soc.,* **47,** 79 (1925); Vorländer, D., *Ber.* **58B,** 2656 (1925); Reggiani, M., *Helv. Chim. Acta,* **15,** 1383 (1932); Qureshi, M., and Mohammad, S. S., *J. Phys. Chem.,* **36,** 2205 (1932); see, however, Dhar, N. R., *J. Chem. Soc.,* **124,** 1860 (1923).

[24] See also Pribram, R., and Franke, A., *Ber.,* **44,** 1035 (1911); *Monatsh.,* **33,** 415 (1912); Akhmatov, A. S., and Baruishanskaya-Landsberg, F. S., *J. Phys. Chem. (U.S.S.R.),* **6,** 83 (1935); *Chem. Abs.,* **29,** 7809 (1935).

[25] Irvine, J. C., and Francis, G. V., *Ind. Eng. Chem.,* **16,** 1019 (1924).

[26] Baly, E. C. C., Davies, J. B., Johnson, M. R., and Shanassy, H., *Proc. Roy. Soc.,* **116A,** 197 (1927); see also Mezzadroli, G., *Rev. ind. agr. Tucumán,* **19,** 154, 526 (1928); *Chem. Abs.,* **23,** 2367 (1929); Mezzadroli, G., and Vareton, E., *Chimie et Industrie,* Special No. 778, March (1931); Mezzadroli, G., and Gardano, G., *Atti acad. Lincei,* **6,** 160 (1927); *Chem. Abs.,* **22,** 760 (1928).

[27] Baly, E. C. C., Stephen, W. E., and Hood, N. R., *Proc. Roy. Soc.,* **116A,** 212 (1927); Baly, E. C. C., *Science,* **68,** 364 (1928); Baly, E. C. C., and Hood, N. R., *Proc. Roy. Soc.,* **122A,** 393 (1929).

[28] Baur, E., and Rebmann, A., *Helv. Chim. Acta,* **5,** 828 (1922).

[29] Baur, E., and Büchi, P. F., *Helv. Chim. Acta,* **6,** 959 (1923).

[30] Burk, D., *J Am. Chem. Soc.,* **49,** 1819 (1927); *Cf.* Ram, A., [*Proc. Acad. Sci., United Provinces Agra Oudh, India,* **4,** 83 (1934); *Chem. Abs.,* **29,** 7383 (1935); Ram, A., and Dhar, N. R., *J. Indian Chem. Soc.,* **15,** 321 (1938); *Chem. Abs.,* **32,** 8941 (1938)] for the alleged production of formaldehyde from many organic compounds by sunlight.

[31] Emerson, R., *J. Gen. Physiol.,* **13,** 163 (1929); see also Baur, E., *Z. physik. Chem.,* **131,** 143 (1928).

[32] Dhar, N. R., and Ram, A., *Nature,* **129,** 205 (1932); *Z. anorg. allgem. Chem.* **206,** 171 (1932); Rao, G. G., and Dhar, N. R., *J. Phys. Chem.* **35,** 1418, 1424 (1931); Dhar, N. R., and Sanyal, R. P., *Ibid,* **29,** 926 (1925).

[33] Dhar, N. R., and Ram, A., *Nature,* **132,** 819 (1933); *J. Indian Chem. Soc.,* **10,** 287 (1933); *Trans. Faraday Soc.,* **30,** 142 (1934); *Nature,* **131,** 800 (1933); *J. Phys. Chem.,* **37,** 525 (1933); Gore, V., *Ibid.,* **39,** 399 (1933).

According to Rajvansi and Dhar,[34] the most effective catalysts for the formation of formaldehyde from carbon dioxide solution in sunlight are manganous chloride and cobalt carbonate, with which a yield of formaldehyde of the order of 0.0005 per cent by volume was claimed. When nascent carbon dioxide was prepared from barium carbonate and hydrogen chloride, formaldehyde was produced by light even in the absence of a photosensitizer. The temperature coefficient of sugar formation in sunlight from a 3-per cent aqueous solution of formaldehyde was found to be 1.2 between 30 and 40°C.

Gore[35] finds that mixtures of tartaric acid and various aldehydes or alcohols in aqueous solutions after exposures to sunlight of 84 or 100 hours without photosensitizers gave positive sugar tests with Benedict's solution. This did not occur in darkness. Gore assumes that light aids the decomposition of tartaric acid by aldehyde to produce nascent carbon dioxide, which reacts with water to produce formaldehyde which polymerizes with the formation of the sugars. It is assumed that when alcohols are used they are first oxidized to aldehydes by light.

Notwithstanding the poor yields that have been reported in all such investigations, Roman[36] patented the production of hexoses and higher carbohydrates by the polymerization of aldehydes, particularly formaldehyde, by light, preferably orange-red. The reaction is said to be best effected in the presence of a compound capable of combining with the carbohydrate, such as an alkaline-earth hydroxide.

In subsequent work, Baly[37] turned to the use of catalysts of ferric oxide supported on kieselguhr previously coated with alumina. The activity was said to be increased by the addition of small quantities of thorium dioxide to the ferric oxide. Bell[38] was unable to confirm these results. Further negative results in the photosynthesis of formaldehyde were also reported by Konstantinova-Shlezinger,[39] and Zscheile[40] reported forty futile attempts to repeat the experiments of Baly with visible light and nickel and cobalt carbonates. He felt that Baly's use of cylinder carbon dioxide may have been a source of organic impurities. Dhar, Rao and Ram[41] claimed success with the use of nickel carbonate and colloidal ferric hydroxide in 2-per cent sodium bicarbonate solutions, notwithstanding Baly's insistence that the catalyst be free from alkali. MacKinney[42] obtained completely negative results with these slightly alkaline catalysts in sunlight or with ultraviolet light between 2900 and 3000A.

Yajnik and Trehana[43] claimed to have verified some of the observations of Baly. White catalysts gave no yield unless artificially colored. The best results were claimed for green, red and blue catalysts, copper arsenate being the most efficient of those tested. Baly[44] recently maintained that it is essential for success that there be a surface which is a true crystal lattice of nickel oxide.

The Physiological Mechanism

Green leaves absorb from 50 to 60 per cent of the incident infrared and approximately 90 per cent of the ultraviolet rays, according to Seybold.[45] In the red region, the maximum absorption by leaves occurs at 6700A. That of an acetone extract of chlorophyll occurs at 6500A. There is a second maximum in the blue-violet, and transmission is greatest in the green. In the living leaf

[34] Rajvansi, A. R., and Dhar, N. R., *J. Phys. Chem.*, **36**, 567, 575 (1932).

[35] Gore, V., *J. Phys. Chem.*, **37**, 745 (1933).

[36] Roman, L. H., German P. 590,236, Jan. 4, 1934; *Chem. Abs.*, **28**, 2013 (1934); Carboxyhyd, A.-G. British P. 374,044 and 458,359.

[37] Baly, E. C. C., *Nature*, **126**, 666 (1930); *Trans. Faraday Soc.*, **27**, 545 (1931).

[38] Bell, J., *Trans. Faraday Soc.*, **27**, 771 (1931).

[39] Konstantinova-Shlezinger, M., *J. Phys. Chem., U.S.S.R.*, **2**, 780 (1931); *Chem. Abs.*, **27**, 5374 (1933).

[40] Zscheile, F. P. Jr., *J. Am. Chem. Soc.*, **54**, 973 (1932).

[41] Dhar, N. R., Rao, G. G., and Ram, A., *Trans. Faraday Soc.*, **27**, 554 (1931); Rao, G. G., and Dhar, N. R., *J. Phys. Chem.*, **35**, 1418 (1931).

[42] MacKinney, G., *J. Am. Chem. Soc.*, **54**, 1688 (1932).

[43] Yajnik, N. A., and Trehana, F. C., *J. chim. phys.*, **28**, 517 (1931).

[44] Baly, E. C. C., *Nature*, **140**, 930 (1937). See also Ostrikov, M. S., *Acta Univ. Voronegiensis*, **9**, No. 3, 95 (1937); *Chem. Abs.*, **32**, 6949 (1938).

[45] Seybold, A., *Planta (Abt. E, Z. wiss. Biol.)*, **21**, 251 (1933); *Chem. Abs.*, **28**, 3758 (1934).

the chlorophyll spectrum is displaced somewhat toward the infrared as compared with that which it exhibits in solution.

Although the carotenes and xanthophyll also make contributions to the absorption of visible light by the leaf, the absorption of chlorophyll is the predominant cause of the color of the leaf.[46]

That chlorophyll may be separated into fractions was suggested by early observers, and confirmed by Willstätter and Stoll.[47] They showed that there are two green pigments chlorophyll-*a* and chlorophyll-*b* present in all plant leaves and separable by a preferential solubility of chlorophyll-*a* in petroleum ether and of chlorophyll-*b* in 90-per cent methanol. In the higher plants there is about three times as much of the former as of the latter.[48]

Wlodek[49] noted that the stripes of the first absorption band, corresponding to both chlorophyll-*a* and *b*, alter in width during exposure of the leaf to light. This indicates either a change in the relative amounts of the two forms of chlorophyll or the appearance of a new type of spectrum due to unstable compounds of chlorophyll with carbon dioxide. Shifts in the situation of the absorption bands of chlorophyll in the presence of certain hydrophilic and lipophilic materials are considered to support a granular model of the chloroplastid by Wakkie.[50]

Action of Light on Chlorophyll. Crude chlorophyll in alcoholic solution was not decomposed by the action of ultraviolet rays in exposures of five to sixty minutes. Bierry and des Bancels[51] found that on prolonged exposures to two mercury arcs, the solutions became faintly yellow and gave positive tests for urobilinogen. A benzene solution of chlorophyll became colorless under these conditions but did not show the color reactions of urobilinogen.[52] According to Dangeard,[53] when light is allowed to fall on a mixture of chlorophyll and Pinaverdol, the former is decolorized. The latter is also attacked and finally destroyed by the light absorbed, not by itself, but by the chlorophyll. It was suggested that the carotene and xanthophylls which accompany chlorophyll in the leaf might also be similarly bleached by the photosensitizing action of chlorophyll.

Bleaching of chlorophyll occurs in the presence of oxygen and of such acceptors as diethylallyl- and diallylthiocarbamide, according to Weber.[54] Ferrous sulfate is also active in neutral or feebly acid solution. In the absence of an acceptor the rate of bleaching is slow. It increases rapidly in the presence of small amounts of acceptor, attains a maximum and diminishes logarithmically with increasing acceptor concentrations. In all cases there is a marked induction period. The rate of bleaching is but little affected by temperature. The bleaching is greatly inhibited by certain phenols, quinones and amines. It is suggested that

[46] The chemistry of chlorophyll has recently been reviewed by Steele, C. C., *Chem. Rev.*, **20**, 1 (1937) and by Fischer, H., *Chem. Rev.*, **20**, 41 (1937).

[47] Willstätter, R., and Stoll, A., "Untersuchungen uber Chlorophyll," Berlin, 1913; transl. by Scherz, F., and Merz, A., Science Publishing Co., 1928.

[48] Their photosynthetic functions have been reviewed by Spoehr, H. A., *Annual Rev. Biochem.*, **2**, 453 (1933) and by Stoll, A., *Naturwiss.*, **24**, 53 (1936).

[49] Wlodek, J., *Bull. Internat. Acad. Pol. Sci. Lettres* **B**, 407 (1924); *Chem. Abs.*, **19**, 2687 (1925).

[50] Wakkie, J. G., *Proc. Acad. Sci. Amsterdam*, **38**, 1082 (1935); *Chem. Abs.*, **30**, 3024 (1936). Methods for measuring the absorption of radiation by leaves are discussed by Mestre, H., *Cold Spring Harbor Symposia Quant. Biol.*, **3**, 191 (1935).

[51] Bierry, H., and des Bancels, J., *Compt. rend.*, **153**, 124 (1911); *J. Chem. Soc.*, **100**, 735 (1911).

[52] See, however, Gouzon, B., *Compt. rend.*, **196**, 1542 (1933).

[53] Dangeard, P. A., *Compt. rend.*, **156**, 1844 (1913).

[54] Weber, K., *Ber.*, **69B**, 1026 (1936); *Nature*, **137**, 870 (1936); Weiss, J., *Nature*, **136**, 794 (1935).

on absorption of a photon a molecule of chlorophyll is so activated as to enable it to combine with a molecule of oxygen, forming a peroxide which then oxidizes the chlorophyll. Induction and after effects are attributed to the long life-periods of the intermediate peroxide. With high acceptor concentrations, chlorophyll is stabilized by the reaction: $AO_2+A \rightarrow 2AO$. According to Porret and Rabinowitsch, the reversible bleaching of chlorophyll is proportional to the square root of the light intensity. It is increased by formic acid and suppressed by ferrous chloride.[55]

An ethylchlorophyllide solution can be reversibly oxidized by ferric chloride to a yellow unstable intermediary product from which the green solution can be regenerated by reduction with ferrous chloride. The oxidation is greatly favored by illumination.[56]

Hubert[57] notes the possibility of the photodecomposition of chlorophyll during the measurement of its absorption spectrum. Suspensoid particles prepared by injecting an acetone solution of chlorophyll into water bear a negative charge which becomes positive after several hours of exposure to light, owing to photoöxidation.[58] Electrical measurements made with metallic plates coated with chlorophyll and illuminated showed in experiments of Dixon and Poole,[59] that the wave-lengths which are effective in photosynthesis are unable to expel electrons from chlorophyll.

Kögel[60] attributes the photosensitivity of chlorophyll to keto-groups. Roffo[61] finds pure chlorophyll strongly photoactive, a property not shared by xanthophyll, phytosterol, carotene or chlorophyllin.

When a hydrazone of phylloerythrin is exposed to light, its spectrum changes to that of phylloerythrin.[62] Etioporphyrin, exposed to sunlight in the presence of oxygen, forms ethylmethylmaleimide, according to Deželić.[63]

Relation of Chlorophyll to Photosynthesis. The importance of chlorophyll in the photosynthetic process is based upon the agreement between the absorption spectrum of chlorophyll and the effective wave-length regions, and also upon the approximate correlation between the photosynthetic activity of partly etiolated plants and their chlorophyll content. The latter agreement is, however, far from an exact one, so it has been suggested that other internal factors may be involved.[64] Studies at various points in the variegated leaves of Pelargonium by Chapman and Camp[65] revealed that no starch is produced in the non-green parts.

Attempts to reproduce the photosynthetic process *in vitro* by the use of extracts of chlorophyll have not yielded promising results. Osterhout[66] sprinkled a carbon tetrachloride solution of chlorophyll on filter paper in amounts sufficient to give it a deep green color. The treated paper was placed in airtight bell jars with large petri dishes containing 5 cc. of water. Some of the sheets were kept

[55] Porret, D., and Rabinowitsch, E., *Nature,* **140,** 321 (1937).
[56] Rabinowitsch, E., and Weiss, J., *Nature,* **138,** 1098 (1936).
[57] Hubert, B., *Proc. Acad. Sci. Amsterdam,* **37,** 684 (1934); *Chem. Abs.,* **29,** 1844 (1935).
[58] Bakker, H. A., *Proc. Acad. Sci. Amsterdam,* **37,** 688 (1934); *Chem. Abs.,* **29,** 1844 (1935).
[59] Dixon, H. H., and Poole, H. H., *Sci. Proc. Roy. Dublin Soc.,* **16,** 63 (1920); *J. Chem. Soc.,* **118,** II, 343 (1920).
[60] Kögel, G., *Strahlentherapie,* **45,** 587 (1932); *Chem. Abs.,* **27,** 2721 (1933).
[61] Roffo, A. H., *Bol. inst. med. exper. cancer Buenos Aires,* **8,** 68 (1931); *Chem. Abs.,* **26,** 5125 (1932).
[62] Fischer, H., Moldenhauer, O., and Süs, O., *Annalen,* **485,** 1 (1931); *Chem. Abs.,* **25,** 1835 (1931).
[63] Deželić, M., *Bull. soc. chim. roy. Yougoslav,* **6,** 11 (1935); *Chem. Abs.,* **29,** 7998 (1935).
[64] Briggs, G. E., *Proc. Roy. Soc.,* **91B,** 249 (1920).
[65] Chapman, A. G., and Camp., W. H., *Ohio J. Sci.* **32,** 197 (1932); *Chem. Abs.,* **26,** 4629 (1932).
[66] Osterhout, W. J. V., *Am. J. Botany,* **5,** 105, 511 (1918); Osterhout, W. J. V., and Haas, A. R. S., *Science,* **47,** 420 (1918).

in darkness and others were placed in light for several days until the chlorophyll had bleached to a pale green color. The water in the dishes kept in darkness gave negative aldehyde tests and that in those in the light gave positive tests. Aniline dyes were believed to behave similarly. Baur[67] embedded the chlorophyll in collodion with an oxidation-reduction system such as methylene blue or iron salts and exposed the layer in water to sunlight. Small quantities of formaldehyde could be detected even when the water had been freed from carbon dioxide. The presence of carotene increases the yield. Dolk and van Veen[68] were unable to reduce carbon dioxide by a protein-containing chlorophyll solution, a reaction previously reported by v. Eisler and Portheim.[69]

In the case of *Pinus Strobus* and *Picea excelsa,* Burns[70] finds wave-length limits for photosynthesis to be 7400 to 4500A approximately. Ursprung[71] found starch formation possible between 7600 and 3300A. Both the red and the blue-violet regions are regarded as necessary for normal photosynthetic activity by Dastur and Mehta.[72] On the basis of equal incident energies at various wave-lengths, Hoover[73] found the entire visible spectrum between 7200-7500A and less than 3650A to be effective. A principal maximum occurred at 6550A in the red and a secondary one at 4400A in the blue. Greater reflection and transmission in the green diminished the effectiveness of these rays. Harder, Döring and Simonis suggest that the assimilatory apparatus of green plants may be able to adapt itself to the wave-length of light in which it is grown.[74]

A new type of starch formation under the influence of wave-lengths shorter than 3000A has been discussed by Richter,[75] who postulates the existence of a chlorophyllase in the leaf to account for his results.

The Mode of Action of Chlorophyll in Photosynthesis. The investigation of the mechanism of the reaction is unfortunately complicated by the necessity for studying it as it occurs in living tissues. Fundamental investigations of the process in leaves were made by Blackman[76] in 1905. These led to a recognition that the rate of the process as conducted under different conditions may be limited by different factors.

Thus, Hoover, Johnston and Brackett[77] find that in wheat, carbon dioxide limits the rate when high light intensities are used, although under conditions of high carbon dioxide concentration, light becomes the limiting factor. In an extensive transition range, both factors may be limiting, in consequence of the wide variation in the illumination and carbon dioxide concentration available for different chloroplasts. Blackman had also called attention to the influence of temperature in altering the nature of the photo-

[67] Baur, E., *Helv. Chim. Acta,* **18,** 1157 (1935); **20,** 387, 391, 398 (1937).
[68] Dolk, H. E., and van Veen, A. G., *Biochem. Z.,* **185,** 165 (1927).
[69] v. Eisler, M., and Portheim, L., *Biochem. Z.,* **135,** 293 (1923).
[70] Burns, G. R., *Science,* **78,** 130 (1933); *Plant Physiol.,* **8,** 247 (1933); **9,** 645 (1934); *J. Am. Chem. Soc.,* **59,** 944 (1937); *Am. J. Botany,* **24,** 257 (1937); *Vt. Agr. Expt. Sta., Bull.* **402,** 2 (1936); *Chem. Abs.,* **31,** 4699, 5020 (1937); *Am. J. Botany,* **25,** 166 (1938).
[71] Ursprung, A., *Ber. deut. botan. Ges.,* **35,** 44 (1917).
[72] Dastur, R. H., and Mehta, R. J., *Ann. Botan.,* **49,** 809 (1935); *Chem. Abs.,* **30,** 503 (1936); see also Dastur, R. H., and Samant, K. M., *Ann. Botan.,* **47,** 295 (1933); *Chem. Abs.,* **27,** 4270 (1933); Dastur, R. H., and Solomon, S., *Ann. Botan.,* **1,** 147 (1937); *Chem. Abs.,* **31,** 2639 (1937).
[73] Hoover, W. H., *Smithsonian Inst. Miscellaneous Collections,* **95,** No. 21 (1937). No increased action due to the joint action of all wave-lengths of white light over that due to the sum of their individual effects occurs, according to Montfort, C., *Ber. deutsch. botan. Ges.,* **55,** 142 (1937); *Chem. Abs.,* **31,** 7089 (1937). An opposite result is noted by Danilov, A. N., *Arch. sci. biol. (U.S.S.R.),* **43,** Nos. 2-3, 365 (1936); *Chem. Abs.,* **32,** 6694 (1938).
[74] Harder, R., Döring, B., and Simonis, W., *Nachr. Ges. Wiss. Göttingen, Math.-physik. Klasse Fach Gruppe,* **VI, 2,** 129 (1936); *Chem. Abs.,* **32,** 7958 (1938).
[75] Richter, O., *Sitzber. Akad. Wiss. Wien, Math. naturw. Kl.,* **I, 144,** 157 (1935); *Chem. Abs.,* **31,** 3762 (1937).
[76] Blackman, F. F., *Proc. Roy. Soc.,* **76B,** 402 (1905); *Ann. Botan.,* **19,** 28 (1905).
[77] Hoover, W. H., Johnston, E. S., and Brackett, F. S., *Smithsonian Miscellaneous Collections,* **87,** 16 (1933); see also Smith, E. L., *J. Gen. Physiol.,* **22,** 21 (1938).

synthetic processes.[78] The temperature of the leaf also alters transpiration, and changes the state of the plasma, alters the ease of penetration of the gases and may have other effects. Furthermore, respiration is also occurring and its effects upon the results require consideration. Dhar[79] suggests that an increase in temperature may affect the respiration more than the photosynthetic process. Another complicating factor is the possibility of the existence of enzymes, which may in some manner be concerned in the process.[80] Various methods of killing leaves affect the photosynthetic process about as do various methods of inactivating enzymes. Inman[81] believes some light-sensitive substance contributes to the production of free oxygen in living but not in dead, plant cell tissues. It is inactivated by trypsin, but not by pepsin, erepsin, amylopsin, diastase, urease or papain. The maximum evolution of oxygen is obtained between pH 5 and 6. The critical temperature for its evolution is 55°C, regardless of pH; that for catalase is 70°C. Wurmser[82] directed attention to the influence of alterations of the cellular reduction potential upon the process. Rhythms in the production and disappearance of starch during 24-hour periods have been observed by Stănescu,[83] who followed quantitatively the variations in the products in the leaves of green plants during the course of a day. The water content of the leaves also exerts a great influence upon the rate of the process.[84] Wood[85] showed that the injection of water into a cherry-laurel leaf lowers its rate of assimilation until nearly all the injected water has disappeared from the intercellular spaces. Dehydration of the leaf by a dry wind[86] retards photosynthesis. Still another factor is the amount of carbohydrate already present.[87]

To avoid so far as possible these many complicating factors some of the investigations which have proved most significant in the interpretation of the mechanism of the process have been conducted on the algae. Warburg and Negelein[88] made a series of observations of the energy exchange in the stems of *Chlorella* using light of four spectral regions. In general the reaction yield decreased with decreasing wave-length, but no relation could be discerned between the yield and the absorption coefficients. The yield in the red, a region of high absorption, was greater than that in the green, a region of very weak absorption, but the yield in the latter case was greater than that in the blue, the region of strongest absorption. The decomposition in the ultraviolet and in the region between 7000 and 7800A could not be accurately determined. There was no utilization of carbon dioxide under the influence of light in the infrared. In *Ulva lactuca,* the yield for equal incident intensities was a maximum in the region in which the chlorophyll absorption was least, according to Wurmser.[89]

Warburg recognized the need for the absorption of several quanta per molecule in order to secure enough energy for the reaction to proceed. The results indicated that four quanta of red or yellow light or five of blue light were required for

[78] Chesnokov, V., and Bazuirina, E. N., *Compt. rend. acad. sci. U.R.S.S.*, **8**, 193 (1930A); *Chem. Abs.*, **25**, 313, 2457 (1931). A review in Russian is given by Nekrasov, N. I., and Krashennikov, F. N., *Uspekhi Khim.*, **6**, 334 (1937).

[79] Dhar, N. R., *J. Indian Chem. Soc.*, **10**, 541 (1933); *Chem. Abs.*, **28**, 2293 (1934); Singh, B. N., and Kumar, K., [*Proc. Indian Acad. Sci.*, **1B**, 736 (1935); *Chem. Abs.*, **29**, 6277 (1935)] consider the effects of temperature on the process in radish leaves.

[80] Molisch, H., cited by Stiles, W., *Scientia,* **41**, 122 (1927); Molisch, H., *Z. Botan.*, **17**, 577 (1925).

[81] Inman, O. L., *Cold Spring Harbor Symposia Quant. Biol.*, **3**, 184 (1935); *Chem. Abs.*, **30**, 7627 (1936).

[82] Wurmser, R., *Compt. rend. soc. biol.*, **95**, 1237 (1926).

[83] Stănescu, P. P., *Ann. Sci. Univ. Jassy,* **14**, 383 (1927); *Chem. Abs.*, **22**, 2390 (1928).

[84] Dastur, R. H., *Ann. Botan.*, **39**, 769 (1925).

[85] Wood, J. G., *Australian J. Exp. Biol.*, **6**, 127 (1929); *Chem. Abs.*, **24**, 1882 (1930).

[86] Skvortzov, S. S., *Bull. Applied Bot., Gen. Plant Breeding, Leningrad,* **25**, No. 3, 45 (1931); *Chem. Abs.*, **26**, 5605 (1932).

[87] Kursanov, A. L., *Planta, Abt. E, Z. wiss. Biol.*, **20**, 535 (1933); *Chem. Abs.*, **28**, 2750 (1934); Spoehr, H. A., and Long, F. L., *Carnegie Inst. Washington, Yearbook,* 17, 60 (1918); Lyubimenko, V. N., *Rev. Gen. Botan.*, **40**, 415, 486 (1928); *Chem. Abs.*, **23**, 412 (1929).

[88] Warburg, O., and Negelein, E., *Z. physik. Chem.*, **106**, 191 (1923).

[89] Wurmser, R., *Compt. rend.*, **177**, 644 (1923); *J. Phys. Radium,* **7**, 33 (1926). The work indicated that Einstein's law did not directly account for the photosynthetic behavior of this sea-weed.

the decomposition of a molecule of carbon dioxide. When corrections were made for the light absorbed by the other photochemically inactive pigments present, it was found that more than three and less than five quanta of blue light were required per molecule of carbon dioxide. The energy efficiency of the total reaction, obtained by dividing 112 kcal. by four times the equivalent energy of the light employed, was found to be 65 per cent for 6600A, 57 per cent for 5780A and 43 per cent for 4360A.

It was also shown in later experiments conducted at very high and at very low light intensities that it is possible to distinguish between the photochemical reaction with low temperature coefficient and a subsequent reaction, called by Warburg the Blackman reaction. This has a higher temperature coefficient and is a thermal reaction.[90] For a given wave-length, the specific photochemical reaction is greater the smaller the intensity, and with very low intensities the action is proportional to the intensity.

Narcotics, such as 0.5×10^{-4} molar phenylurethane, powerfully inhibited both the photochemical and the Blackman reactions. Hydrogen cyanide and hydrogen sulfide, however, inhibited only the Blackman reaction.

Considerable information has been yielded by studies of the effect of intermittent light. By using a rotating sector, Brown and Escombe[91] found that three-quarters of the light from a given source could be cut out in each revolution of the sector without decreasing the rate of photosynthesis by leaves. Willstätter attributed this to the slowness of the diffusion of carbon dioxide to the cells during the dark period. In Warburg's experiments with light of high intensity and with a high concentration of carbon dioxide, it was found that even in algae, a given amount of light reduced more carbon dioxide when applied intermittently than when the illumination was continuous. The increase in the yield depended upon the frequency of the flashing. It was 10 per cent with four periods per minute and 100 per cent with a frequency of 8000 per minute. Emerson and Arnold[92] believed that certain steps in the Blackman reaction proceed during the dark period. When the light intensity is high, the initial photochemical reaction is capable of proceeding at great speed. In continuous light, however, it can go no faster than the Blackman reaction. Since it seemed likely that in the latter, chlorophyll is regenerated, it may be that the Blackman reaction limits the rate of the photochemical process. Higher efficiency of utilization of the light would be obtained if each flash lasted only long enough to build up the equilibrium concentration of intermediate products and each dark period were long enough to allow the slower Blackman reaction time to use up all the intermediate products present at the end of the light period. By using only fifty flashes per second and making the flashes much shorter than the dark periods, Emerson and Arnold were able to increase the yield by 300 to 400 per cent of that under continuous illumination. The necessary dark period varied from about 0.03 to 0.4 second, depending on the temperature. The light period could be reduced to 0.00001 second. The light reaction is dependent upon the carbon dioxide concentration and is inhibited by narcotics. They differed from Warburg in not finding the dark reaction inhibited by narcotics, although it is inhibited by cyanides. It is independent of the carbon dioxide concentration. From the speed of the light reaction, it was suggested that a chlorophyll-carbon dioxide complex may be activated to form molecules capable of undergoing the Blackman reaction.

[90] Warburg, O., *Biochem. Z.*, **166**, 386 (1925); **100**, 230 (1919); **103**, 188 (1920).

[91] Brown, H. T., and Escombe, F., *Proc. Roy. Soc.*, **76B**, 29 (1905). For reviews, see Briggs, G. E., *Biol. Review Cambridge Phil. Soc.*, **10**, 460 (1935); Emerson, R., *Enzymforsch.*, **5**, 305 (1936).

[92] Emerson, R., and Arnold, W., *J. Gen. Physiol.*, **15**, 391 (1931-2); **12**, 623 (1929). There is no similarity between the Blackman reaction and the decomposition of hydrogen peroxide by *Chlorella,* according to Emerson, R., and Green, L., *Plant Physiol.*, **12**, 537 (1937).

From studies on several higher plants, Briggs [93] concluded that, contrary to the results of Warburg and Negelein, the number of quanta required for the production of a molecule of carbon dioxide increases discontinuously with increasing wave-length. In the case of spruce, Burns [94] found the relative number of quanta required per molecule of carbon dioxide to be 9.5, 10 and 5 for the wave-length regions 7200-6300A, 7200-5600A and 4700-3900A. Thus the quantum yields were much smaller than those found by Warburg. Recently, Manning, Stauffer, Duggar and Daniels [95] reported that an extensive series of investigations had failed to confirm the quantum yield for *Chlorella* reported by Warburg as 0.25. Instead, the value was much lower, 0.05, and in some experiments, particularly those with higher light intensities, was still lower, even approximating zero. No explanation of the discrepancy could be advanced. It was pointed out that the Warburg results indicated a high enough efficiency in the utilization of the energy [96] for it to be profitable to attempt formulations of the mechanism of the coupled reactions which occur. The newer low quantum yields, however, make possible a large number of conceivable mechanisms, and leave our knowledge of the nature of this fundamental reaction in a chaotic state. Only a brief discussion will, therefore, be given of a few of the mechanisms which have been suggested.[97]

The mechanism suggested by Willstätter and Stoll was based upon their belief that carbon dioxide reacts with chlorophyll-*a* to form a carbon dioxide-chlorophyll complex of the same color as chlorophyll.[98] The absorption of light was thought to convert this into an isomer of peroxide-like nature. This is capable of liberating oxygen and an oxymethylene group with regeneration of chlorophyll.[99] Several observations by Warburg lent support to this theory. *Chlorella* in 0.03 molar hydrogen peroxide solution in darkness evolved the same amount of oxygen as does the same amount of the irradiated algae in the Blackman reaction. The effects of temperature, hydrogen cyanide and narcotics on the Blackman reaction and the evolution of oxygen from hydrogen peroxide by *Chlorella* were similar.

Photosynthesis occurs in the absence of oxygen in at least 14 species of marine algae. Within a second of the illumination, oxygen is liberated and may be detected by its action on luminous bacteria.[100] This is confirmed by Gaffron.[101] Carbon monoxide influences the process, possibly by an action on an enzyme assumed to control the liberation of oxygen in the Blackman reaction. Kohn [102] finds that iodoacetic acid and its amide inhibit photosynthesis by attacking the Blackman reaction.

Ostwald [103] suggested the possibility of a primary photoactivation to a lipoid peroxide at an interface between lipoid and protein, the assumed reaction being in some manner promoted by chlorophyll, which was not thought to enter directly into the mechanism.

[93] Briggs, G. E., *Proc. Roy. Soc.*, **105B**, 1 (1929); *Brit. Chem. Abs.* **A**, 960 (1929).

[94] Burns, G. R., *Plant Physiol.*, **8**, 247 (1933); *Chem. Abs.*, **27**, 3239 (1933).

[95] Manning, W. M., Stauffer, J. F., Duggar, B. M., and Daniels, F., *J. Am. Chem. Soc.*, **60**, 266 (1938); Manning, W. M., Juday, C., and Wolf, M, *ibid.*, 274; *Trans. Wis. Acad. Sci.* **31**, 377 (1938).

[96] Adams, E. Q., interprets the results as indicating an efficiency of 98.6 per cent [*J. Am. Chem. Soc.*, **48**, 292 (1926)] if the fundamental reaction is assumed to be $CO_2 + 3H_2O \rightarrow HCHO + 2H_2O_2$.

[97] Pfeilsticker, K., *Biochem. Z.*, **199**, 12 (1928) applied stereochemical ideas to the theory of photosynthesis.

[98] Willstätter, R., and Stoll, A., *Ber.*, **50**, 1791 (1917); see also Peklo, J., *Chem. News*, **129**, 90 (1924).

[99] An earlier theory of Willstätter, since discarded, assumed a participation of xanthophyll and carotene. See also Heilbron, I. M., *J. Soc. Chem. Ind.*, **43**, 89T (1924); *Chem. Abs.*, **15**, 3072 (1921).

[100] Harvey, E. N., *Plant Physiol.*, **3**, 85 (1928); *Chem. Abs.*, **23**, 185 (1929).

[101] Gaffron, H., *Biochem, Z.*, **280**, 337 (1935).

[102] Kohn, H. I., *J. Gen. Physiol.*, **19**, 23 (1935).

[103] Ostwald, Wo., *Kolloid-Z.*, **33**, 356 (1923).

Attention was also devoted to the possibility that light enables the chlorophyll in some manner to split hydrogen from water, producing hydrogen peroxide. Thunberg [104] suggested that hydrogen, carbon dioxide and water might react to produce oxygen and H_4CO_2, the latter breaking down to formaldehyde and water. Weigert [105] suggested that in an internal photoelectric effect in a chlorophyll-water complex, the passage of an electron from the pigment to the water with the production of a hydrogen atom and hydroxyl ion may occur. Two hydroxyl ions might then form hydrogen peroxide, returning the electrons to chlorophyll molecules.

Shibata and Yakushiji [106] suggest that the chlorophyll-carbonic acid complex binds four water molecules coördinatively to the magnesium atom. The absorption of four quanta activates the water molecules of the complex forming four hydrogen atoms and four hydroxyl groups. The hydrogen atoms react with carbonic acid with the formation of formaldehyde and two molecules of water. The four hydroxyl radicals form two molecules of hydrogen peroxide which are subsequently decomposed to water and oxygen by the leaf catalase. The catalase poison, hydroxylamine, added in low concentrations, inhibits the liberation of oxygen and changes assimilation into respiration. This theory was developed particularly to account for the now disputed quantum yield of 0.25.

Kögel [107] believed that chlorophyll activates the carbon dioxide and forms $(OH)_2C(OH)_2$ as the initial product.

Kautsky and Hirsch [108] studied the changes in the fluorescence of chlorophyll in leaves during exposure to light. The intensity of the fluorescence rises rapidly to a maximum (one second) and then slowly drops (four minutes) to a low value, which thereafter remains constant. At O°C., or after the addition of hydrogen cyanide, the initial rise still occurs but there is no subsequent decrease. It is suggested that the period of falling fluorescence intensity represents an induction period during which the Blackman reaction occurs. Normal assimilation is assumed to occur on the final weak fluorescent level of the curve for the fluorescence intensity at various times during irradiation. The steep initial rise in the curve, which is independent of temperature or cyanide, increases with the light intensity. It is ascribed to the establishment of the photochemical equilibrium:

$$\text{Chlorophyll-}CO_2 + h\nu \rightleftarrows \text{Chlorophyll-formaldehyde peroxide.}$$

The fluorescence is largely inhibited by oxygen.[109] The absorption of a quantum by the pigment system [110] activates it so that it fluoresces intensely. The fluorescence may then be quenched by the transfer of the excitation energy to an unidentified compound containing loosely bound molecular oxygen, designated $A(O_2)$. This energy (about 37 kcal. or a little less than the red fluorescence, 42 kcal.) stabilizes the oxygen compound. The energy-transfer is a surface phenomenon, which can be abolished by such a surface-active substance as phenylurethane. The stable excited oxygen compound is changed back to the dissociable one in the chloroplasts by a

[104] Thunberg, T., *Z. physik. Chem.*, **106**, 305 (1923). A substance liberating iodine from potassium iodide is said to be formed when leaves of sugar cane (also stalks and roots) are exposed to sunlight. Fujii, M., and Nishioeda, M., *Rept. Gov. Sugar Expt. Sta., Tainan, Formosa*, No. 5, 47 (1938); *Chem. Abs.*, **32**, 8487 (1938).

[105] Weigert, F., *Z. physik. Chem.*, **106**, 313 (1923).

[106] Shibata, K., and Yakushiji, E., *Naturwiss.*, **21**, 267 (1933); Yakushiji, E., *Acta Phytochim.*, **7**, 93 (1933); *Chem. Abs.*, **27**, 4269 (1933).

[107] Kögel, G., *Naturwiss.*, **19**, 571 (1931).

[108] Kautsky, H., and Hirsch, A., *Naturwiss.*, **19**, 964 (1931); Kautsky, H., and Spohn, H., *Biochem. Z.*, **274**, 435 (1934); **277**, 250 (1935).

[109] Kautsky, H., Hirsch, A., and Davidshöfer, F., *Ber.*, **65**, 1762 (1932); *Chem. Abs.*, **27**, 1029 (1933); Dastur, R. H., and Desai, B. L., [*Annal. Botan.*, **47**, 69 (1933)] interpret the curves for fluorescence on the basis of a double photo-reaction involving, first the activation of carbon dioxide and second, the decomposition of water.

[110] Kautsky, H., and Hirsch, A., *Biochem. Z.*, **274**, 423 (1934). For recent studies of fluorescence in *Chlorella*, see Wassink, E. C., Vermeulen, D., Reman, G. H., and Katz, E., *Enzymologia*, **5**, 100, 110 (1938).

heavy metal catalyst, liberating oxygen, energy and the substance A. The latter again combines with molecular oxygen. It is this reaction which depends upon temperature and which is inhibited by cyanides. The energy liberated in the breakdown of the oxygen compound is utilized in the reduction of carbon dioxide.

That the dehydrogenation of chlorophyll may play a part in the photosynthetic process was suggested by Conant, Dietz and Kamerling.[111] In a dark enzymatic process, six molecules of carbon dioxide may remove two hydrogen atoms from each of twelve chlorophyll molecules forming a hexose, six molecules of water and twelve of dehydrochlorophyll. In a subsequent photochemical reaction, chlorophyll is regenerated by abstracting hydrogen from water, releasing its oxygen.

On the basis of some observations by Stoll,[112] Willstätter [113] altered the Conant concept of the process. In place of assuming that the hydrogen atoms of chlorophyll are lost as a pair in its dehydrogenation, he considered them to transfer separately, monodehydrochlorophyll thus acting as an intermediary compound. It is formed by the action of an oxygen molecule upon chlorophyll and is converted into dehydrochlorophyll by the transfer of its hydrogen atom to the magnesium carbonic acid complex. Then, in light, the dehydrochlorophyll, acting with water, reforms monodehydrochlorophyll and the hydroxyl radical. The former then again transfers its hydrogen to the magnesium-carbonic acid complex and the resulting dehydrochlorophyll again absorbs light. After the transfer of four hydrogen atoms to the magnesium complex with carbonic acid, the dehydro- and monodehydro-compounds are reconverted into chlorophyll by the light reaction and by a reaction in which water and monodehydrochlorophyll form the hydroxyl radical and chlorophyll.

Franck[114] believed that the Willstätter mechanism, with monodehydrochlorophyll as the significant compound, could be altered slightly to correspond to the energy yields of the reaction and with the data of the Kautsky fluorescence curves. The initial rise in the Kautsky curve corresponds to a photo-process in which hydrogenated chlorophyll gives monodehydrochlorophyll and atomic hydrogen, the latter reacting with oxygen and water to give hydrogen dioxide. The photochemical yield of this reaction is poor. The subsequent drop in the fluorescence corresponds to a process in which monodehydrochlorophyll reacts with carbon dioxide with the production of hydroxychlorophyll and formic acid. In subsequent reactions in light, monodehydrochlorophyll, formaldehyde and hydrogen peroxide are produced. During the slow dark reaction, the original hydrogenated chlorophyll is reformed. It will be noted that the Franck theory assumes a photo-dissociation of a lightly bound hydrogen atom from chlorophyll. The recombination of this hydrogen atom produces a chemiluminescence of the same color as that of the fluorescence. It is, therefore, possible to determine from the fluorescence wave-length limits the energy required for the separation of the hydrogen atom. From the long wave-length limit of the narrow fluorescent band at 6800A, this is concluded to be 41.4 kcal.

The reactions of the Franck preparatory photoprocesses are written:

(1) $HH\text{—Chlorophyll} + h\nu \longrightarrow H\text{-Chlorophyll} + H.$

(2) $H + O_2 \longrightarrow O_2H$

(3) $O_2H + H_2O \longrightarrow H_2O_2 + OH$

(4) $OH + OH \longrightarrow H_2O_2.$

[111] Conant, J. B., Dietz, E. M., and Kamerling, S. E., *Science*, **73**, 268 (1931).
[112] Stoll, A., *Naturwiss.*, **20**, 955 (1932).
[113] Willstätter, R., *Naturwiss.*, **21**, 252 (1933).
[114] Franck, J., *Naturwiss.*, **23**, 226 (1935); *Chem. Rev.*, **17**, 443 (1935).

The equations for the assimilation process proper are written:

(1) $\text{H—Chlorophyll} + \text{HC(OH)}_2\text{=O} + h\nu \longrightarrow \text{OH—Chlorophyll} + \text{HC(OH)H=O}$

(2) $\text{OH—Chlorophyll} + \text{HC(OH)}_2\text{=O} + H_2O + h\nu \longrightarrow \text{H—Chlorophyll} + \text{HC(OH)}_2\text{=O} + H_2O_2$

(3) $\text{H—Chlorophyll} + \text{HC(OH)}_2\text{=O} + h\nu \longrightarrow \text{OH—Chlorophyll} + \text{HC(H)}_2\text{=O}$

(4) $\text{OH—Chlorophyll} + H_2O + h\nu \longrightarrow \text{H—Chlorophyll} + H_2O_2.$

These equations were held to be energetically possible. In (1) and (3), light causes a change in position of an hydroxyl group of the bound carbonic or formic acid with a hydrogen atom of chlorophyll. In each case the hydrogen atom is the more firmly bound.

As to the possibility of reactions (2) and (4) it is said that it is necessary to supply enough energy to dissociate water into H and OH and in addition to separate the OH from the chlorophyll residue. The former requires 115 kcal. and the latter about 20 kcal., assuming the hydroxyl group to be at most half as firmly bound as the hydrogen on chlorophyll. There are available 41 kcal. by absorption of a quantum, and the same amount by the binding of a hydrogen atom on the chlorophyll residue and finally 52 kcal. from the combination of two hydroxyl groups to hydrogen peroxide. The new feature in the Franck formulation is the production of the more loosely bound OH-chlorophyll; this was believed to overcome the energetic difficulties in the previous formulation of the mechanism by Willstätter.

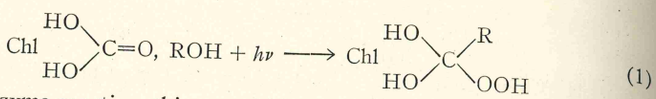
Oxygen is assumed necessary only for the preparatory processes. In its absence, irradiation would lead to the production of some carbon dioxide and the strongly fluorescent dehydrochlorophyll. This was believed to lose its energy by fluorescence most readily. This was held to explain the Kautsky curves in the absence of oxygen in which the fluorescence rose rapidly to a maximum after which it remained constant. Kautsky,[115] however, states that his curve of this type was obtained in the presence of small amounts of oxygen, but not in its absence. When oxygen was absent, he could observe no fluorescence. Moreover, Kautsky maintains that his conception of the processes is in agreement with the work of Warburg on the separation of the process into a photochemical one and the Blackman reaction.

The study of fluorescence spectra has been extended to that of pheophorbide-*b* by Knorr and Albers,[116] who follow its change during irradiation in the presence of various gases, oxygen, nitrogen and carbon dioxide.

Wohl [117] shows that the energy of four quanta of 6800A, light which still gives photosynthesis, is smaller than the energy difference between the initial and final

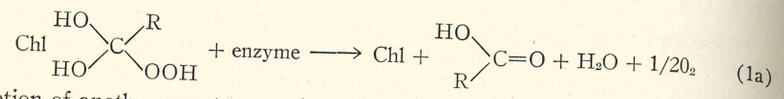
[115] Kautsky, H., *Naturwiss.*, **23**, 389 (1935); Kautsky, H., and Flesch, W., *Biochem. Z.*, **284**, 412 (1936); Kautsky, H., and Marx, A., *Naturwiss.*, **24**, 317 (1936); *Biochem. Z.*, **290**, 248 (1937); Kautsky, H., and Hormuth, R., *Naturwiss.*, **24**, 650 (1936); *Biochem. Z.*, **291**, 285 (1937); Kautsky, H., *Ibid.*, **291**, 271 (1937).
[116] Knorr, H. V., and Albers, V. M., *Phys. Rev.*, **47**, 329 (1935); *Cold Spring Harbor Symposia Quant. Biol.*, **3**, 87, 98 (1935).
[117] Wohl, K., *Z. physik. Chem.*, **31B**, 152 (1935); see also Gaffron, H., and Wohl, K., *Naturwiss.*, **24**, 81, 103 (1936).

products of the overall reaction for the Franck mechanism, 192 kcal. At 6600A four quanta give 172 kcal. Franck and Herzfeld[118] suggest that for such a fluorescent, polyatomic molecule as chlorophyll, which has many degrees of freedom, the missing 20 kcal. may be supplied from the thermal energy. Franck has subsequently altered his suggested mechanism.[119] The preparatory reaction was shown unnecessary by Gaffron.[120] The assumption of hydrogen peroxide is avoided in Franck's most recent mechanism. The chlorophyll-carbonic acid complex is assumed to be attached to an organic molecule ROH. The absorption of a quantum is thought to convert this into a peracid.



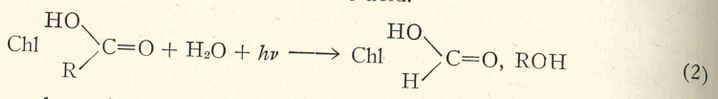
(1)

In a thermal enzyme reaction, this peracid is converted into an acid with liberation of oxygen.



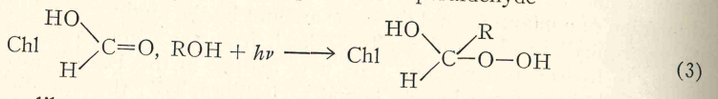
(1a)

Absorption of another quantum produces formic acid.



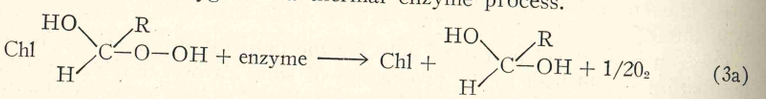
(2)

This in turn on absorption of a quantum produces a peraldehyde



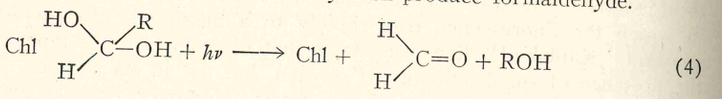
(3)

which may then liberate oxygen in a thermal enzyme process.



(3a)

The aldehyde on absorption of a quantum may then produce formaldehyde.



(4)

It is not possible in a limited space to discuss the mathematical developments of these reactions made by Franck, and their application to the rapidly accumulating body of experimental data. Gaffron suggests that a free-moving enzyme of the Blackman reaction forms in the dark an inactive dissociable oxygen compound. The complex can be activated by excess light energy when in a reducing location. He believes this may explain the observed rapid oxygen consumption directly after intensive illumination, and the high temperature coefficient of the induction.[121]

Wohl gives reasons for believing the Franck and Herzfeld reaction chain

[118] Franck, J., and Herzfeld, K. F., *J. Phys. Chem.*, **41**, 97 (1937); Franck, J., *J. Wash. Acad. Sci.*, **27**, 317 (1937).

[119] Franck, J., and Herzfeld, K. F., *J. Chem. Physics*, **5**, 237 (1937).

[120] Gaffron, H., *Naturwiss.*, **23**, 528 (1935).

[121] Gaffron, H., *Naturwiss.*, **25**, 460 (1937); *Chem. Abs.*, **31**, 8557 (1937); *Naturwiss.*, **25**, 715 (1937); *Chem. Abs.*, **32**, 2977 (1931).

mechanism kinetically impossible.[122] It is recently suggested by Baas-Becking and Hanson[123] that in the chloroplast the chlorophyll molecules occur in planes and are oriented in tetrads with the pentanon ring of each pointing to the same center, and that orthocarbonic acid is fixed at this center by the active hydrogen atoms of the four chlorophyll molecules.

Knoll, Matthews and Crist regard the Blackman reaction as an enzymatic decomposition of a peroxide formed in the photo-process. They find it the rate-determining process in the oxygen evolution at high light intensities and high carbon dioxide concentrations.[124]

Because of their highly controversial and speculative nature, further consideration of the details of theories of the photosynthetic mechanism must be left to the specialist in this most important field.

Photosynthetic Units. In intermittent light experiments on cells with varied chlorophyll content, Emerson and Arnold[125] showed that for every 2480 molecules of chlorophyll one molecule of carbon dioxide was reduced in a single flash. This means either that the quantum efficiency is very low or that most of the light is absorbed by chlorophyll molecules not in contact with carbon dioxide. The suggestion was made that 2480 molecules function as a unit to reduce one molecule of carbon dioxide. The mean time for a unit to complete the cycle of photochemical and Blackman reactions was calculated to be between 0.01 and 0.02 second. The existence of such a photosynthetic unit was subsequently detected in work on six plant species.[126] More recently, Kohn[127] by measuring the oxygen production on exposure of green algae to flashes from a neon tube found only 360 molecules of chlorophyll to comprise the photosynthetic unit. Weiss[128] accounts for the existence of the unit by assuming that about 500 molecules in the interior of a lipoid phase absorb and hand on the necessary quanta for one molecule on the surface. He also believes ferrous ions at the surface play a role in the reduction. It may be noted that Franck regards the assumption of photosynthetic units as unnecessary. Weiss also discusses the mode of transfer of excitation energy from molecule to molecule in the complex.[129]

Important studies have recently been made on the course of photosynthesis in certain purple bacteria which promise to throw some light on the evolution of photosynthetic mechanisms. Van Niel[130] observed that some of these organisms require the absorption of but one quantum. On the other hand, French[131] states that the process is similar to that in green plants. Recently, the quantum yield has been found to be much lower, twelve to eighteen quanta (8500-8900 or 5900A) being required to reduce a molecule of carbon dioxide.[132]

The possibility that a chromoprotein as phycoerythrin may act as the sensitizer in the red algae has been discussed by Wurmser[133] and by Moore, Whitley and

[122] Wohl, K., *Z. physik. Chem.*, **B37**, 122, 169 (1937).

[123] Baas-Becking, L. G. M., and Hanson, E. A., *Proc. Acad. Sci. Amsterdam*, 40, 792 (1937); *Chem. Abs.*, **32**, 2178 (1938).

[124] Knoll, A. F., Matthews, F. L., Jr., and Crist, R. H., *J. Chem. Phys.*, **6**, 109 (1938). For recent kinetic data on photosynthesis, especially the induction period, in single fronds of *Cabomba caroliniana*, see E. L. Smith, *J. Gen. Physiol.*, **20**, 807 (1937); **21**, 151 (1937).

[125] Emerson, R., and Arnold, W., *J. Gen. Physiol.*, **16**, 191 (1932).

[126] Arnold, W., and Kohn, H. I., *J. Gen. Physiol.*, **18**, 109 (1934); see also Arnold, W., *Ibid.*, **17**, 135 (1933).

[127] Kohn, H. I., *Nature*, **137**, 706 (1936) .

[128] Weiss, J., *J. Gen. Physiol.*, **20**, 501 (1937). See also Wohl, K., *Z. physik. Chem.*, **B37**, 105, 186, 209 (1937).

[129] Weiss, J., *Nature*, **141**, 248 (1938).

[130] Van Niel, C. B., *Cold Spring Harbor Symposia Quant. Biol.*, **3**, 138 (1935); *Chem. Abs.*, **30**, 6782 (1936); Gaffron, H., *Biochem. Z.*, **275**, 301 (1935); van Niel, C. B., *Bull. assoc. diplomes microbiol, faculte pharm. Nancy*, **No. 13**, 3 (1936); Sapozhnikov, D. I., *Biokhimiya*, **2**, 181 (1937); *Chem. Abs.*, **31**, 7923 (1937).

[131] French, C. S., *Science*, **84**, 575 (1936); *J. Gen. Physiol.*, **21**, 71 (1937). See also Nakamura, H., *Acta Phytochim. (Japan)*, **9**, 189, 231 (1937); *Chem. Abs.*, **31**, 7465 (1937); *Acta Phytochim. (Japan)*, **10**, 211 (1937); *Chem. Abs.*, **32**, 210 (1938).

[132] Eymers, J. G., and Wassink, E. C., *Enzymologia*, **2**, 291 (1938); *Chem. Abs.*, **32**, 5436 (1938).

Webster.[134] Montfort [135] finds fucoxanthin in brown algae to have a definite physiological function in increasing the photosynthetic efficiency in blue light. Instead of falling off from the red to the blue, it increases in some species to a value three times as high as required by the quantum theory and to more than twice the efficiency in red light. Carotene and xanthophyll in plants in which they are present appear not to have a part in increasing the efficiency.[136] In *Chlorella*, respiration and photosynthesis are retarded by 88 per cent heavy water.[137] Pratt, Craig and Trelease [138] found that although 99.9 per cent heavy water depressed photosynthesis to 41 per cent of that in water in bright light, it showed little difference from water at low light intensities. The lower rate suggested that deuterium exchanges for hydrogen at a critical point in some molecule involved in one of the dark reactions. The respiration is less retarded by heavy water. The temperature coefficients of photosynthesis in H_2O and D_2O were the same in the range 10-30 °C, but higher for D_2O than water between 30 and 46 °C.

Plane-polarized light formed no different amount of starch from that produced by ordinary light in the leaves of *Allium cepa* or *Helianthus annuus*.[139] On the other hand, elliptically polarized light retarded the formation of carbohydrates in leaves.[140] Leaves were also said to absorb a larger amount of energy from polarized than from ordinary light.

It has been suggested that ester formation in plants is due to the ultraviolet rays of sunlight.[141] Pal [142] finds light necessary for not only the conjugation of *Spirogyra*, but also for the conversion of carbohydrates to fats or oils. In darkness, there occurs a conversion of fats to carbohydrates. Our knowledge of the photosynthesis of volatile oils and allied principles is still speculative.[143]

Photosynthesis of Proteins. Baly, Heilbron and Hudson [144] reported that activated formaldehyde, produced photochemically according to the disputed methods of Baly, reacts rapidly with nitrites with the formation of hydroxamic acid, the reaction taking precedence over the polymerization of the formaldehyde to reducing sugars.[145] Formhydroxamic acid is assumed by Baly to react further in various ways with activated formaldehyde to give rise to α-amino acids and nitrogen bases, including even alkaloids. Baly and co-workers believed they had isolated two alkaloids and an amino-acid like histidine formed in this manner in *in vitro*

[133] Wurmser, R., *Trav. Inst. Physiol. Gen. Strassbourg*, 1919-20; *Chem. Abs.*, **19**, 3289 (1925).

[134] Moore, B., Whitley, E., and Webster, T. A., *36th Ann. Report. Oceanography, (Liverpool)* 1922; *Chem. Abs.*, **19**, 3289 (1925).

[135] Montfort, C., *Jahrb. wiss. Botan.*, **83**, 725 (1936); *Chem. Abs.*, **31**, 4693 (1937); Schmidt, G., *Jahrb. wiss. Botan.*, **85**, 554 (1937); *Chem. Abs.*, **32**, 3788 (1938).

[136] See, however, Sapozhnikov, D. I., *Biokhimiya*, **2**, 730 (1937); *Chem. Abs.*, **32**, 6673 (1938).

[137] Shibata, K., and Watanabe, A., *Acta Phytochim.*, **9**, 107 (1936); *Chem. Abs.*, **30**, 8272 (1936).

[138] Pratt, R., Craig, F. N., and Trelease, S. F., *Science*, **85**, 271 (1937); *Am. J. Botan.*, **24**, 232 (1937); Curry, J., and Trelease, S. F., *Science*, **82**, 18 (1935); Pratt, R., and Trelease, S. F., *Am. J. Botany*, **25**, 133 (1938).

[139] Dastur, R. H., and Asana, R. D., *Ann. Botany*, **46** 879 (1932); *Chem. Abs.*, **27**, 2709 (1933); Johnston, E. S., *Smithsonian Inst. Pub. Misc. Collections*, **96**, No. 3 (1937).

[140] Dastur, R. H., and Gunjikar, L. K., *Ann. Botan.*, **48**, 1003 (1934); **49**, 273 (1935); *Chem. Abs.*, **29**, 1456, 5877 (1935). See, however, Semmens, E., *Nature.*, **134**, 813 (1934); **130**, 243 (1932); *Bot. Gaz.*, **90**, 412 (1930); *Chem. Abs.*, **25**, 983 (1931).

[141] Stoermer, R., and Ladewig, H., *Ber.*, **47**, 1804 (1914).

[142] Pal, N. L., *New Phytol.*, **33**, 242 (1934); *Chem. Abs.*, **29**, 2997 (1935).

[143] Singleton, F., *Chem. & Ind.*, **50**, 989 (1931).

[144] Baly, E. C. C., Heilbron, I. M., and Hudson, D. P., *J. Chem. Soc.*, **121**, 1078 (1922); *J. Soc. Chem. Ind.*, **41**, 609A (1922); *Chem. Abs.*, **16**, 3463 (1922); Baly, E. C. C., Heilbron, I. M., and Stern, H. J., *J. Chem. Soc.*, **123**, 185 (1923); *Chem. Abs.*, **17**, 1421 (1923).

[145] Either diffused daylight or ultraviolet, according to Baudisch, O., [*Ber.*, **44**, 1009 (1911); **49**, 1176 (1916); **51**, 793 (1918)] causes methanol to react with potassium nitrite, yielding the potassium salt of formhydroxamic acid, CHOH=NOK.

experiments. Snow and Stone,[146] however, pointed out that the identification of these alkaloids had been insufficient, and that certain simpler compounds would yield the tests which had been described.

Burk [147] made over five hundred experiments to detect the formation of complex nitrogen compounds by the action of intense sunlight and colored inorganic catalysts upon ammonia and such carbon compounds as carbon dioxide, formic acid, formaldehyde or dextrose. The results were in general negative. The only type of reaction observed was the oxidation of ammonia to nitrate which occurred in the presence of ferric chloride, or to nitrites and nitrates in the presence of zinc or mercuric oxide. Hydroxylamine and hydrogen peroxide, or complex nitrate compounds were never produced.

Recently, however, Bhargava and Dhar,[148] claimed success in the production of nicotine and methylamine by exposing a small quantity of ammonia and a 2 per cent solution of formaldehyde to a mercury-vapor lamp or to sunlight in the presence of zinc oxide, titanium dioxide or copper carbonate. Dhar and Mukherjee [149] also claimed that a similar exposure of 0.5N solutions of ammonium, potassium or sodium nitrate, containing glucose, tartaric acid, glycerol, arabinose, fructose, mannose or galactose, gave positive colorimetric tests for amino-acids. The yields were best with ammonium nitrate and none were formed in darkness or when ammonium hydroxide was used as the nitrogen source. The amounts of amino-acids reached a maximum in four to six hours, after which they were removed by oxidation.

Urban [150] finds that ammonia nitrogen is taken up by *Chlorella* and other forms more rapidly in light. Loose and Pearsall [151] find that in this organism the velocity of protein synthesis is five times as great in light as in darkness. If sufficient carbohydrate is available, the final equilibrium is similar.[152]

According to Tottingham and Louwsma,[153] a 50 to 400 per cent increase in the blue, violet and long ultraviolet rays increases the absorption of nitrates and to a smaller extent the synthesis of proteins by wheat. When the short wave-length limit is extended from 4000 to 3700A, there is no change. When it is extended to 3000A there is an increase in the absorption but not in the assimilation of nitrates. The admission of rays as short as 2800A decreases the formation of tissue and proteins. Although increasing the proportion of blue to violet light by supplementing Mazda lamps by carbon arcs increases the percentage of protein in young wheat plants, it decreases the pentosans and crude fiber.[154] Solar ultraviolet causes more marked changes and increases the percentage of lipids and of uronic acid.

In tobacco stalks and leaves, light probably leads to a synthesis of glutamine.

[146] Snow, O. W., and Stone, J. F. S., *J. Chem. Soc.*, **123**, 1509 (1923); *Chem. Abs.*, **17**, 2865 (1923).

[147] Burk, D., *J. Phys. Chem.*, **31**, 1338 (1927). See also Calcagni, G., *Rev. biol.*, **22**, 92 (1937); *Chem. Abs.*, **32**, 4625 (1938).

[148] Bhargava, L. N., and Dhar, N. R., *J. Indian Chem. Soc.*, **10**, 453 (1933); *Chem. Abs.*, **28**, 413 (1934).

[149] Dhar, N. R., and Mukherjee, S. K., *Nature*, **134**, 499 (1934); *J. Indian Chem. Soc.*, **11**, 727 (1934); *Chem. Abs.*, **29**, 2450 (1935).

[150] Urban, O., *Jahrbuch Wiss. Botan.*, **75**, 1 (1932); *Chem. Abs.*, **26**, 4629 (1932).

[151] Loose, L., and Pearsall, W. H., *Nature*, **171**, 362 (1933).

[152] For the blue-green alga, *Nostoc*, see Allison, F. E., and Hoover, S. R., *Trans. 3rd Intern. Congress Soil Sci. Oxford*, **1**, 145 (1935); *Chem. Abs.*, **29**, 8203 (1935).

[153] Tottingham, W. E., and Louwsma, H. W., *J. Am. Chem. Soc.*, **50**, 2436 (1928); Tottingham, W. E., Stephens, H. L., and Lease, E. J., *Plant Physiol.*, **9**, 127 (1934); *Chem. Abs.*, **28**, 3444 (1934).

[154] Tottingham, W. E., and Lease, E. J., *Science*, **80**, 615 (1934); *J. Am. Chem. Soc.*, **57**, 2613 (1935).

Malic acid diminishes and citric acid increases in cultures in darkness. Oxalic acid is unchanged.[155]

Small amounts of ultraviolet light cause an increase in the nitrogen content of *Sinapis alba*.[156]

[155] Vickery, H. B., Pucher, G. W., Wakeman, A. J., and Leavenworth, C. S., *Conn. Agr. Expt. Sta., Bull.* **407,** 111 (1938); *Chem. Abs.*, **32,** 5441 (1938); *J. Biol. Chem.*, **119,** 369, 523 (1937).

[156] Kabos, W. J., *Rec. trav. botan. neerland.*, **33,** 447 (1936); *Chem. Abs.*, **32,** 212 (1938).

Chapter 44

Effects of Ultraviolet Radiations on Plants

Although de Lima [2] found that ultraviolet light has no effect on germinating rye, others have claimed that, at least in certain wave-length regions, it stimulates germination. DeWolf and Fry [3] proposed to subject seeds before sowing to the action of ultraviolet rays from a mercury-vapor lamp or other source, with or without previous treatment in water or a solution of sodium nitrate or manure. Heinisch [4] believed the germinating power of unripe barley to be considerably improved by ultraviolet irradiation. If, however, the same barley had been allowed to ripen before harvesting, the effect of irradiation was less striking.

Many workers have, however, shown that in general unfiltered mercury arc irradiations are harmful to germinating plants. In the case of dry seeds, lack of penetration of the coats may prevent these effects from becoming readily apparent. There is general agreement that if radiations of wave-length shorter than 2900A are applied, lethal action will result, as discussed in Chapter 33 in the case of bacteria and other organisms.[5]

Some authors have recently claimed that there is a stimulating action of ultraviolet rays longer than the lethal limit. Higgins and Sheard [6] found wave-lengths between 3200 and 3900A transmitted by a Corning ultraglass filter 586 AW, particularly effective in producing germination and growth of cucumber seeds. Rays between 2700 and 3200A delayed the time of germination and reduced the rate of growth.

Gilles [7] believed the germination of lentil and turnip seeds accelerated but their growth somewhat diminished by mercury-arc irradiation. A few other workers claimed to have obtained a stimulating action by filtered ultraviolet, applying wave-lengths in the region of 3650A or those of daylight.[8]

These reports have been criticized by Popp and Brown,[9] largely because the

[1] The interested reader may find summaries of the extensive work on the effects of visible light in the book edited by Duggar, B. M., "Biological Effects of Radiation," New York, McGraw-Hill Book Company, Inc., 1936.

[2] de Lima, P., *Compt. rend.*, **105,** 493 (1930).

[3] De Wolf, C. E., and Fry, H. E., British P. 23,339, Oct. 15, 1913; *Chem. Abs.*, **9,** 950 (1915).

[4] Heinisch, O., *Wochschr. Brau.*, **49,** 348 (1932); *Chem. Abs.*, **27,** 3028 (1933); de Fazi, R., *Atti Acad. Lincei*, **11,** 1022 (1930); *Chem. Abs.*, **25,** 3121 (1931); Kamenskii, K. V., and Orekhova, T. A., *Bull. Applied Botany, Genetics Plant Breeding (U.S.S.R.), Ser.* **IV,** No. 2, 67 (1937); *Chem. Abs.*, **31,** 5843 (1937).

[5] Carl, *Beitr. Biol. Pflanz. (Cohn's)*, **12,** 435 (1914); Sibilia, C., *Bull. soc Bot. Ital.*, 160 (1925) cited by Popp, H. W., and Brown, F., in Duggar, B. M. "Biological Effects of Radiation," New York, McGraw-Hill Book Co., Inc., 1936, II, Chapter 26. Dane, H. R., *Science*, **66,** 80 (1927); Delf, E. M., Ritson, K., and Westbrook, A., *Brit. J. Exptl. Biol.*, **5,** 138 (1927); Cluzet, J., and Kofman, T., *Compt. rend. soc. biol.*, **101,** 820 (1929).

[6] Higgins, G. M., and Sheard, C., *Plant Physiol.*, **2,** 325 (1927); *Chem. Abs.*, **22,** 3685 (1928).

[7] Gilles, E., *Compt. rend. soc. biol.*, **109,** 739 (1932); *Chem. Abs.*, **27,** 3969 (1933). Gilles reviews work subsequent to 1881 and concludes light less than 2900A favors germination, but affects adult plants adversely. The range 2900 to 3100A favors plant development. *Ann. univ. Lyon, Ser. 3,* **1C,** 38 (1936); *Chem. Abs.*, **32,** 7965 (1938).

[8] Valentin, H., *Pharm. Ztg.*, **75,** 982, 995, 1005 (1930); *Chem. Abs.*, **25,** 120 (1931); Jacobi, *Beitr. Biol. Pflanz. (Cohn's)*, **16,** 405 (1928); Masure, M. P., *Botan. Gaz.*, **93,** 21 (1928); *Chem. Abs.*, **26,** 2487 (1932).

[9] Popp, H. W., and Brown, F., *Bull. Torrey Botan. Club*, **60,** 161 (1933); *Chem. Abs.*, **27,** 2709 (1933); "Biological Effects of Radiation," edited by Duggar, B. M., **II,** 851, New York, McGraw-Hill Book Company, Inc., 1936.

possible effects of infrared rays upon the irradiated plants were not adequately eliminated. Very extensive studies by Popp led to the following generalizations:[10]

1. Exposure of dry seeds to the full ultraviolet of a quartz mercury-vapor arc have little or no effect on later germination and growth, even after 188 hours' exposure. This may be due to inability of the short rays to penetrate the dry seed coat.

2. Exposures of less than two hours' duration on soaked seeds that have not yet begun to sprout did not have a marked effect on germination. Probably here too there is not enough penetration of the short rays in so short a time to cause any permanent injury.

3. Longer exposures to the open arc decrease the rate and the amount of germination, inhibit growth and development and finally cause death of the plant. The wavelengths below 3000A are more effective in this respect than are those above.

4. In general, cotyledons of seeds exposed to ultraviolet seems to have difficulty in emerging from the seed coat, but if they do get through they are not seriously injured by the short rays until after long exposures, 120 hours.

5. Chlorophyll appears in the cotyledons of seedlings raised under the open arc about as rapidly as it does in ordinary light, but never reaches the intensity it does in daylight.

6. Ultraviolet light does not seem to be necessary for a development of the reddish-purple pigment on the under side of the cotyledons of mustard. Under Noviol glass which screens off all ultraviolet and in the dark, this pigment always appears. It reached its deepest intensity uniformly in the greenhouse plant where comparatively little ultraviolet was present.

7. Geranium plants exposed to the open arc for 6 hours, after being in the dark for 24 hours showed no difference in appearance at the end of the 6 hours, but tests of the leaves for starch at this time were entirely negative. But in ordinary light, starch can be located in these leaves after an hour or less.

8. In no case were new leaves formed in mustard under ultraviolet rays. The new leaves were formed in sunflower, Canada field peas, oats and corn, but these leaves were all killed in a day or two after they were formed.

9. A few plants were able to grow under the open arc in all of the series but in no case was there any further development than would result from the food stored in the seeds.

10. Seedlings that do not survive will live longer under its rays than those grown in the dark at the same time. Since there is apparently very little food synthesis, this may be due to a retarding of enzyme action or other germination processes. If these seedlings after being exposed from 6 to 8 hours a day for 10 to 15 days are removed to the greenhouse, they immediately start to develop normally; but exposed seeds that have not germinated under ultraviolet rays cannot be made to germinate in this way later.

11. Seedlings grown in daylight in the absence of ultraviolet or in complete darkness and then exposed to the open arc were killed after 6 to 20 hours' exposure. Similarly, the leaves of mature plants of geranium or coleus with 6 hours' exposure to the open arc will have a burnt appearance the next day and fall off. In the seedlings, the young leaves and next the stems are most susceptible to injury. Apparently, those grown under the arc from the start are able to adapt themselves to it to a certain extent. Finally, of course, they too are killed.

12. When all ultraviolet was screened off, mustard seeds in visible light gave as high a rate and amount of germination as they did in complete darkness. This same effect was produced, however, when the seeds were exposed to all the rays between 6000 and 3000A. If the ultraviolet between 3000 and 4000A was the only radiation falling on the seeds, a somewhat lower rate and amount of germination were observed. Apparently, the inimical effects of the regions between 4000 and 3000A are overcome when visible light is falling on the plants at the same time.

13. No striking differences in growth and development of seedlings of mustard were observed when all ultraviolet was screened off, as compared with seedlings grown under the rays from 6000 to 3000A. If, however, the region between 4000 and 3000A was the only one to which the seedlings were exposed, a distinct retarding of growth and development occurred.

14. Bacteria and general damping-off fungi do not develop in the rays of the open arc but will if the region below 3000A is screened off.

[10] Private communication from Prof. H. W. Popp.

More Mature Plants. A large number of investigations have been devoted to the determination of the effects on growth which may be ascribed to the ultraviolet portion of the solar spectrum. Maquenne and Demoussy[11] early stated that ultraviolet rays properly applied are very beneficial to flowers and other vegetation. In various species, Tottingham and Moore[12] found seed production, root storage or earliness of blooming were favored by irradiation under Vitaglass as compared with common glass. Certain species which do not possess winter hardening capacities were more subject to frost injury following early development under this glass. In some instances an increase in the percentage of protein or non-protein, non-lipid nitrogen was found in the tissues produced under Vitaglass. The most consistent compositional response to this irradiation was believed to be an increased percentage of lipids in the dry matter, but this was not very definite. Similar results were also reported for tomato seedlings by Tottingham,[13] using a General Electric sunlamp. Popp[14] believes that, although ultraviolet rays are not indispensable, the blue-violet end of the visible spectrum is necessary for the normal, vigorous growth of the plant.

Subsequently, Popp and Brown[15] reviewed a number of papers in which a stimulating effect of the ultraviolet longer than 2900A had been claimed. It is scarcely necessary to discuss these here. In practically all of them it was possible to find flaws in the methods employed. Arthur,[16] at the Boyce Thompson Institute was unable to find that the use of ultraviolet-transmitting glasses offered any advantages in plant growth.

Singh, Kapoor and Choudhri[17] found exposure of plants to ultraviolet rays for periods of five minutes or more at intervals of less than 14 days to be detrimental to growth.

Ultraviolet produces growth inhibition and morphological changes in Aspergillus, according to Kresling and Shtern.[18]

The growth substance, 3-indolepropionic acid, turns yellow under ultraviolet irradiation and acquires an unpleasant odor. At the same time the blue fluorescence of its acid solutions decreases, as does its ultraviolet absorption band. After several hours of irradiation, the solution loses its ability to retard the root growth of corn and bean roots in Knop's solution.[19] Similarly, the growth substance in oat coleoptiles loses its activity when intensely irradiated with a mercury arc.[20]

The formation of chlorophyll is favored by visible light of low intensities; high intensities of light tend to destroy it. Relatively few observations have been made on the influence of ultraviolet light upon its formation. According to Tottingham,[21] tomato leaf tissue grown under glass and under Vitaglass showed respectively,

[11] Maquenne, L., and Demoussy, E., *Compt. rend.*, **149,** 756 (1909).

[12] Tottingham, W. E., and Moore, J. G., *J. Agr. Research,* **43,** 133 (1931); *Chem. Abs.,* **25,** 5913 (1931).

[13] Tottingham, W. E., *Plant Physiol.,* **7,** 551 (1932).

[14] Popp, H. W., *Am. J. Botan.,* **13,** 706 (1926); *Chem. Abs.,* **22,** 3191 (1928); *Botan. Gaz.,* **82,** 306 (1926); *Chem. Abs.,* **21,** 435 (1927). See also Arthur, J. M., and Harvill, E. K., *Contrib. Boyce Thompson Inst.,* **8,** 433 (1937); *Chem. Abs.,* **31,** 6285 (1937).

[15] Popp, H. W., and Brown, F., "Biological Effects of Radiation," edited by Duggar, B. M., II, 853; New York, McGraw-Hill Book Company, Inc., 1936.

[16] Arthur, J. M., *Sci. Monthly,* **31,** 343 (1930); Arthur, J. M., and Newell, J. M., *Am. J. Botan.,* **16,** 338 (1929).

[17] Singh, B. N., Kapoor, G. P., and Choudhri, R. S., *Botan. Gaz.,* **97,** 649 (1936); *Chem. Abs.,* **30,** 4197 (1936).

[18] Kresling, E. K., and Shtern, E. A., *Zentr. Bakt. Parasitenk.,* **II Abt. 95,** 327 (1936); *Chem. Abs.,* **30,** 5256 (1936).

[19] Hare, D., and Kersten, H., *Plant Physiol.,* **12,** 509 (1937).

[20] Burkholder, P. R., and Johnston, E. S., *Smithsonian Misc. Coll.,* **95,** No. 20 (1937).

[21] Tottingham, W. E., *Science,* **75,** 223 (1932); *Chem. Abs.,* **26,** 2488 (1932).

chlorophyll 1.76 and 1.50 per cent, carotene, 0.007 and 0.017 per cent, and xanthophyll 0.053 and 0.368 per cent. From the lipid fraction, there were obtained sterols to the extent of 0.81 and 0.87 per cent. The conclusion was that the formation of carotenoids and sterols is favored by irradiation under Vitaglass, but the chlorophyll declines. The ratio of chlorophyll-*a* to chlorophyll-*b* is lowered by irradiating leaves with monochromatic light largely absorbed by chlorophyll-*a*.[22]

Colla [23] ascribes the formation of chlorophyll in wheat, beans and lentils to the action of radiations in the range 3300 to 3900A, without the aid of visible rays.

Stoklasa [24] early observed that after irradiation by wave-lengths 3000 to 5000A (mercury arc), the young leaves of the etiolated seedlings of *Pisum, Zea mais, Avena* and *Hordeum* showed a dark green coloration in two hours. With solar irradiation a similar color was formed only after six hours of exposure. He also believed that chlorophyll exerts a protective action against ultraviolet rays of daylight. The cells of flowers as well as those of plants grown under glass were more sensitive toward ultraviolet rays than the cells of green leaves. Jirovec [25] finds the chlorophyll-free stems of *Euglena gracilis* considerably more sensitive to ultraviolet rays than are green stems of the same species. Dangeard [26] found the energy of wave-lengths shorter than 4900A from a Nernst lamp incapable of aiding the formation of chorophyll, but Sayre [27] has found that if the intensity is high enough chlorophyll may be developed by the wave-length region 3000 to 4000A. The function of the ultraviolet is still, however, uncertain.[28]

A colorless protochlorophyll may be present in sunflower seedlings grown in the dark, but etiolated plants must be irradiated before chlorophyll can form in them.[29] Beck finds that xanthophyll and carotene are formed in the dark. However, light may stimulate the production of these pigments.[30]

Certain acid-fast bacteria produce pigment in darkness only after brief preceding exposures to ultraviolet light or longer exposures to incandescent lamp light.[31]

Wave-lengths in the region 2900 to 3100A were believed by Benedict [32] to increase the dry weights of a number of plants, but not of corn. They also cause an increase in the calcium content, but the results with phosphorus were inconclusive. Wynd and Fuller [33] observed that when tomato and cucumber plants were irradiated daily through Vitaglass at 100 inches from an arc, after five weeks there was an increase in the calcium content as compared with that in controls. The phosphorus content decreased. Experiments of this type were conducted

[22] Tottingham, W. E., and Dutton, H. J., *Science,* **87,** 214 (1938).

[23] Colla, S., *Boll. soc. ital. biol. sper.,* **4,** 298 (1929); *Chem. Abs.,* **23,** 4496 (1929).

[24] Stoklasa, J., *Strahlentherapie,* **6,** 119 (1915); *Zentr. Biochem. Biophys.,* **18,** 370 (1915).

[25] Jirovec, O., *Protoplasma,* **21,** 577 (1934); *Chem. Abs.,* **28,** 6765 (1934).

[26] Dangeard, P. A., *Botaniste,* **12,** xxii (1912). Cited in Duggar, B. M., "Biological Effects of Radiation," New York, McGraw-Hill Book Co., Inc., 1936.

[27] Sayre, J. D., *Plant Physiol.,* **3,** 71 (1928).

[28] See also Shirley, H. L., *Am. J. Botany,* **16,** 354 (1929).

[29] Beck, W. A., *Studies Inst. Divi Thomae,* **1,** 109 (1937); *Protoplasma,* **28,** 273 (1937); *Plant Physiol.,* **12,** 885 (1937); Vogele, A. C., *Ibid.,* **12,** 929 (1937).

[30] Beck, W. A., *Studies Inst. Divi Thomae,* **1,** 217 (1937); Beck, W. A., Redman, R., and Schroeter, M. P., *Ibid.,* **1,** 245 (1937). See also Seybold, A., and Egle, K., *Planta,* **28,** 87 (1938); *Chem. Abs.,* **32,** 5443 (1938); Strain, H. H., *Plant Physiol.,* **13,** 413 (1938); *Chem. Abs.,* **32,** 8476 (1938); Strott, A., *Jahrb. wiss. Botan.,* **86,** 1 (1938); *Chem. Abs.,* **32,** 8482 (1938).

[31] Baker, J. A., *J. Bact.,* **35,** 625 (1938).

[32] Benedict, H. M., *Botan. Gaz.,* **96,** 330 (1934); *Chem. Abs.,* **29,** 1131 (1935).

[33] Wynd, F. L., and Fuller, H. J., *Ann. Mo. Botan. Gardens,* **18,** 565 (1931); *Chem. Abs.,* **26,** 2215 (1932).

to determine whether sterols in the plant could be converted into a vitamin which aids the absorption of calcium by the plant as in the case of vitamin D in animals. According to Stewart and Arthur,[34] tomato, tobacco, datura, lettuce, and salvia, grown in periods of low light intensity and then irradiated by a quartz mercury arc, showed an increase in ash, and in calcium or phosphorus or both. If, however, the plants were grown in light of high intensity, they failed to exhibit these changes on irradiation. Cabbage did not show these changes. It responded at first by an increase in ash in the leaves and a decrease in the stem. Repeated irradiations caused an increase of ash of stem and leaves and an increase in calcium or phosphorus or both. The manganese and magnesium contents of plants were not affected by ultraviolet irradiation. Similar ash changes could be obtained by treating the plants with irradiated ergosterol.

Tomato plants previously grown on solutions lacking calcium or phosphorus showed no increase in ash, calcium or phosphorus on irradiation with a quartz mercury arc. The level of the supply of these elements and not their ratio determines the response to irradiation. In solutions low in phosphorus and high in calcium, irradiation increases the ash and calcium. In solutions low in calcium and high in phosphorus, the ash and phosphorus increased.[35]

In experiments of Mitchell,[36] equal amounts of radiant energy from a 3000-watt carbon arc and a 2000-watt Mazda incandescent lamp were supplied for two weeks to tomato plants. Those under the arc grew less in height and synthesized more than twice as much solid matter and approximately four times as much acid-hydrolyzable materials and sugars as did those under the incandescent lamp. For equal incident energy, the arc was 53 per cent more efficient in electrical energy consumption in producing dry matter. But when the light from the two sources was balanced by a photronic cell, there was a more equal gain in dry weight and carbohydrates under both sources. Those plants under the arc then synthesized less solid matter per unit of time than did those under the incandescent lamp.

But little work has been done on the effect of ultraviolet on the respiration of plants. Masure [37] claimed that the region near 3650A, obtained by the use of a Corning G586AW filter, temporarily accelerates the respiration of pea seedlings. His work has, however, been criticized by Popp and Brown [38] on the ground that the filter used transmitted also infrared radiations and that these, rather than the ultraviolet, may have been the cause of the effects observed. Wynd, Fuller and Reynolds [39] believe that injurious raying of tomato plants stimulates respiration and peroxidase and, in general, catalase, but inhibits oxygenase. Non-injurious raying stimulated catalase. Comparatively weak irradiation of bean plants stimulated peroxidase.

Percival [40] finds that exposure to light coming through window glass causes a darkening of the mycelium of the fungus, *Fomes pini.* Exposures to ultraviolet rays of sunlight in addition to the visible spectrum caused a further darkening

[34] Stewart, W. D., and Arthur, J. M., *Contrib. Boyce Thompson Inst.,* **6,** 225 (1934); *Chem. Abs.,* **28,** 5853 (1934).

[35] Stewart, W. D., and Arthur, J. M., *Contrib. Boyce Thompson Inst.,* **9,** 105 (1937); *Chem. Abs.,* **32,** 1756 (1938).

[36] Mitchell, J. W., *Botan. Gaz.,* **99,** 412 (1937); *Chem. Abs.,* **32,** 1759 (1938).

[37] Masure, M. P., *Botan. Gaz.,* **93,** 21 (1932); *Chem. Abs.,* **26,** 2487 (1932).

[38] Popp, H. W., and Brown, F., *Bull. Torrey Botan. Club,* **60,** 161 (1933); *Chem. Abs.,* **27,** 2709 (1933).

[39] Wynd, F. L., Fuller, H. J., and Reynolds, E. S., *Ann. Missouri Botan. Gardens,* **22,** 837 (1935); *Chem. Abs.,* **30,** 3466 (1936).

[40] Percival, W. C., *Bull. N. Y. State Coll. Forestry,* **6,** IB, 72 pp. (1933); *Chem. Abs.,* **29,** 2573 (1935).

of the mycelium and a suppression of aerial hyphae. Stephens [41] finds ultraviolet irradiation of certain strains of the fungus *Glomerella* greatly stimulated conidial production. Certain strains which had never been known to produce perichecia did so after irradiation if either pepsin, raffinose or magnesium sulfate was added to the nutrient medium.[42]

Some applications of ultraviolet light in the treatment of plant diseases have been noted by Pichler and Wöber,[43] but x-rays were more efficient.

Attempts are being made in the U.S.S.R. to induce the formation of rubber in plants by treating them with ultraviolet rays. Novikov and Herber [44] soaked seeds of the Tau-sagyz rubber plant in distilled water for 18 hours at 25°C., dried and irradiated them with a quartz mercury arc under varying conditions. After irradiation, the seeds were allowed to germinate at 25°C. for two days, after which the catalase activity was determined. In all irradiated seeds the catalase activity increased abruptly. Ultraviolet irradiation of the leaves of Tau-sagyz and Asclepias, previously saturated with 3-per cent sucrose solutions, caused these plants to continue the formation of rubber in the dark in a 3-per cent sucrose solution. Non-irradiated leaves, either saturated or unsaturated with sugar, not only formed no new rubber in the dark but even lost that which they had contained. Irradiated leaves not saturated with sugar did not produce any rubber.

During growth, plants from irradiated seeds were said not to have been attacked by aphids; they also shed their leaves later and recovered their foliage earlier, indications of increased life tonus.

From microchemical observations, Kiselev, Osipov and Kuz'mina,[45] concluded that the formation of rubber and closely related resinous material is a photosynthetic process.

Exposure of apples to ultraviolet light produced injury and discoloration of the anthocyanins, according to Pearce and Streeter.[46] Freytag [47] finds that ultraviolet rays may produce necrotic pigmentation (probably melanin) in leaves and fruit skins. Oxygen is necessary for this. With certain leaves a change in permeability seems to result.

No significant increase in the glucoside yield could be obtained by growing digitalis plants under glass transparent to ultraviolet rays, according to recent experiments of Leonard and Arthur [48] which thus failed to confirm the prior claims of McCrae that this could be done.[49]

Potato tubers irradiated for twenty days with a Uviol mercury arc or by Mazda lamps showed an increased solanine content, accompanied by the appearance of anthocyanin in the sprouts. Irradiation with red-orange light did not induce a significant increase in solanine but caused an increase in chlorophyll. Ultraviolet rays of about 3000A were believed to be effective in solanine formation.[50]

[41] Stephens, F. L., *Philippine Agr.*, **19**, 265 (1930); *Chem. Abs.*, **25**, 1274 (1931).

[42] For data on cells of the prothallium of *Osmundia claytoniana* or *Pteris longifolia*, see Charlton, F. B., *Am. J. Botany*, **25**, 431 (1938).

[43] Pichler, F., and Wöber, A., *Centr. Bakt. Parasitenk., II*, **57**, 319 (1922); *Chem. Abs.*, **17**, 1270 (1923).

[44] Novikov, V. A., and Herber, E. K., *Compt. rend. Acad. Sci. U.R.S.S.*, 131 (1933); *Chem. Abs.*, **28**, 1740 (1934).

[45] Kiselev, N. N., Osipov, A. P., and Kuz'mina, K. A., *Bull. Acad. Sci. U.R.S.S., Classe sci. math. Nat.*, **9**, 1367 (1935); *Chem Abs.*, **29**, 5481 (1935).

[46] Pearce, G. W., and Streeter, L. R., *J. Biol. Chem.*, **92**, 743 (1931); see also Colla, S., *Boll. Soc. ital. biol. sper.*, **4**, 298 (1929); *Chem. Abs.*, **23**, 4496 (1929).

[47] Freytag, H., *Botan. Centr. Beihefte*, **51**, 408 (1933); *Chem. Abs.*, **28**, 504 (1934).

[48] Leonard, C. S., and Arthur, J. M., *J. Am. Pharm. Assoc.*, **23**, 224 (1934).

[49] McCrae, A., *Science*, **71**, 346 (1930).

[50] Conner, H. W., *Plant Physiol.*, **12**, 79 (1937); *Chem. Abs.*, **31**, 5017 (1937).

Results on the effect of ultraviolet rays on the changes in water, total and reducing sugars, and malic acid during the ripening of green-picked apples, peaches, pears and plums were irregular, according to Leonicini and Rogai.[51] In some experiments, the total sugar was reduced (one-tenth to one-sixth) by irradiation.

Ultraviolet light (particularly of wave-length 2980A) causes browning of banana skins exposed in air but not in pure carbon dioxide. The effect is inhibited by hydrogen cyanide for wave-lengths less than 3200A, but the effect of the 3800A line is activated by a little hydrogen cyanide and inhibited by an excess. Enzymes of respiration may be involved in the effects.[52]

[51] Leonicini, G., and Rogai, F., *Ann. sper. agrar, (Rome)*, **21**, 108 (1936); *Chem. Abs.*, **31**, 8731 (1937).

[52] Haussen, I., *Naturwiss.*, **26**, 136 (1938); *Chem. Abs.*, **32**, 6270 (1938).

Author Index

Abbot, C. G., 1, 192, 196, 197, 714
Abderhalden, E., 670, 674, 675, 677, 709, 756, 766
Abe, G., 757
Abe, T., 764
Abel, E., 248, 447
Abelous, 432
Abrahamowicz, J., 657
Abram, H. H., 148
Ackerson, C. W., 814
Acly, H. E., 431
Adam, A., 793, 821
Adam Hilger, Ltd., 853
Adam, N. K., 804, 811
Adams, D. R., 763, 764
Adams, E. Q., 93, 738, 876
Adamson, D. W., 460
Adel, A., 194
Aden, T., 369
Adkins, H., 805
Adler, E., 686
Afzelius, I., 358
Agarbiceanu, T., 273
Agduhr, E., 822
Agnew, M. C., 824
Agnew, R. G., 824
Agren, G., 689
Agulhon, H., 680
Ahier, G., 189
Ahrens, F., 601, 610
Ahrens, G., 810
Aicher, J., 142
Aickin, R. G., 291
Aikins, G. A., 761
Akiyama, M., 706
Akmatov, A. S., 869
Albanese, G., 646
Albela, D., 757
Albers, H., 683
Albers, V. M., 50, 271, 879
Albertal, M., 744
Albert Meyer-Sans Boeuf Co., 613
Alberts, H., 632
Albu, H. W., 355, 357
Albus, G., 742
Alekseevskii, E. V., 392, 460
Alexander, 100
Algerino, A., 647
Ali, M., 358
Alink, R., 648
Alius, H. J., 741
Allen, A. J., 72, 382, 674
Allen, E., 689
Allen, R. P., 248
Allenbach, 780
Allin, E. J., 155
Allingham, J., 662
Allison, F. E., 883
Allmand, A. J., 107, 108, 246, 252, 255, 284, 287-291, 297, 298, 346, 347, 357, 439, 441, 442, 443, 446
Almasy, F., 161, 314, 466, 473, 690
Almquist, H. J., 670, 856
Aloy, J., 407, 432, 525
Aloy, R., 525
Alpatov, D. M., 494
Alpatov, V. V., 717
Alphen, H. C., 35
Altenburg, J., 688
Alterthum, H., 47
Altschuller, M. M., 756
Alverdes, F., 684
Alyea, H. N., 356, 410
Amagat, P., 467
Amatore, G., 646
Ambroglio, A., 861
American Tobacco Co., 660
Ames, F. B., 836
Ammann, H., 364
Ammann-Brass, H., 364
Ammon, R., 553
Amoreux, G., 671
Amrhein, F. J., 847
Amy, L., 188
Anand, H. L., 267
Andant, A., 108, 434, 456, 665
Anderson, A. K., 840
Anderson, C. N., 659
Anderson, E. G. E., 268
Anderson, G. M., 824
Anderson, H., 650
Anderson, J. A., 35, 40
Anderson, K. D., 461
Anderson, L. C., 476, 626
Anderson, N. J., 60
Anderson, P. G., 824
Anderson, R. J., 792, 795
Anderson, S. H., 46, 47
Anderson, W. R., 284
Anderson, W. T., Jr., 74, 79, 80, 97, 103, 105, 126, 131, 133, 135, 268, 340, 352, 636, 735
Ando, T., 817
Andraschko, E., 521
Andre, M., 516
Andrejeff, I., 299
Andresen, O., 835
Andresen-Kraft, C., 156, 171
Andrews, R. S., 661
Andrews, W. S., 38, 164, 189
Andrich, K., 182, 331, 545
Andrik, L., 759
Angeletti, A., 474
Angelica, V., 860
Angenot, P., 521
Anger, V., 519
Angström, A., 193
Angus, T. C., 806
Ankinovich, A. G., 625
Antropoff, A. von, 366
Ansbacher, S., 852
Anschütz, 453
Anslow, G. A., 673
Anslow, W. P., 407
Anson, M. L., 676
Aoki, M., 350
Appel, W. D., 622, 636, 637, 638, 640, 642, 643
Appelmans, R., 711
Appleyard, E. T. S., 7
Appleyard, M., 429
Arago, F., 4
Ardenne, M. von, 142
Arend, A. G., 645
Arends, B., 425, 428, 437, 441, 458, 671, 674
Arens, H., 380, 381, 384
Ariga, T., 628
Arloing, S., 692
Armand-Delille, P., 770
Armour, R. W., 280
Armstrong, H. E., 497
Armstrong, R. T., 395, 466
Arnold, H. D., 49
Arnold, R. B., 723
Arnold, W., 695, 875, 881
Arnone, M., 57
Arnone, V., 57
Arnow, L. E., 629, 671, 674
Arnulf, A., 193
Arny, H. V., 657
Arons, 66
Arrhenius, S., 209, 377
Arro, H., 630
Arthur, J. M., 712, 887, 889, 890
Arthus, M., 678, 691
Arwentiew, B., 494
Asada, T., 74, 116
Asahina, T., 670, 674
Asahina, Y., 506
Asami, Y., 40
Asana, R. D., 882
Asano, K., 601, 605, 606
Ashdown, A. A., 395, 466
Asher, D. W., 819
Ashkenaz, E. W., 760
Ashley, S., 280
Ashton, L. O., 841
Ashton, M. R., 682, 711, 716
Ashworth, J. R., 196
Askew, F. A., 511, 801, 804, 805, 806, 821
Asperger, H., 740
Astbury, W. T., 679
Asterblum, M., 629
Aston, F. W., 227, 366, 614
Astrove, P. S., 847
Asundi, R. K., 53, 331
Aten, A., 206, 299
Athanasiu, G., 105, 106
Athias, F., 405
Atkins, W. R. G., 103, 108
Atlas Electric Devices Co., 578
Atsuki, K., 617
Aubel, E. v., 293
Aubert, M., 467
Auchinachie, D. W., 818
Audubert, R., 101, 210, 339, 387
Auer, L., 558, 573
Auerbacher, L. J., 835
Augustine, J., 743
Auhagen, E., 805, 807, 821
Austen, R., 35
Austin, P. R., 548
Auwers, K. von, 500, 806, 810
Avakova, E. S., 652
Avery, W. H., 355
Avramenko, L., 243
Axilrod, B. M., 411
Axmann, 66, 74
Ayrton, Mrs. H., 46, 47
Ayyar, P. R., 541
Azuma, T., 124
Azuma, Y., 760
Azzi, A., 865

Baas-Becking, L. G. M., 881
Baba, H., 389
Babasaki, Y., 825
Babcock, H. D., 50
Bach, A., 868
Bach, H., 774
Bacharach, A. L., 785, 814
Bachem, A., 735, 739
Bacher, R. F., 27

Bachhaus, A. A., 662
Bachmann, P., 73
Bachmann, W. E., 476, 477
Baciu, A., 490
Backer, H. J., 413
Backès, M., 416
Bacon, H. E., 322
Bacon, R. E., 443
Badertscher, A. E., 658
Badger, R. M., 280, 536
Badische Anilin und Soda Fabrik, 173, 533
Badoche, M., 423, 510, 511
Badstübner, W., 425
Badzynski, S., 513
Bäckström, H., 178, 187, 356, 357, 422, 423, 473
Baeder Illatszergyar R. T., 847
Bänninger, A., 415
Bär, F., 851, 852
Bär, R., 82
Baeyer, A. von, 867
Bagdasar'yan, K. S., 381
Bagnall, H. H., 104
Bahr, E. V., 297
Bailey, A. A., 711
Bailey, A. C., 709
Bailey, C. H., 723, 830
Bailey, K. C., 358
Baird, 73, 78
Baird and Tatlock, 103
Baker, F. E., 659
Baker, H. B., 286, 299, 376
Baker, J. A., 888
Baker, S. L., 711
Bakker, H., 618, 872
Balada, A., 655
Balakhovskiĭ, S., 740
Balandina, V., 605
Balard, A., 305
Balderrey, F. C., 747, 753, 772
Baldini, V., 474
Baldwin, W. M., 764
Balezin, P., 837
Balinkin, I. A., 68
Balls, S. F., 139
Balmer, 20, 22
Balsac, F. de, 817
Baltes, J., 565
Baly, E. C. C., 49, 152, 209, 214, 218, 228, 267, 268, 271, 287, 368, 866, 868, 869, 870, 882
Bamberger, E., 496
Bamberger, P., 821, 839
Bamford, C. H., 422, 425, 429
Ban, N., 829
Bancels, J. des, 871
Bancels, L. des, 585
Bancroft, W. D., 248
Bandel, G., 575
Bandow, F., 665
Banerjee, B. N., 856
Banerjee, S., 682, 684
Banerjee, T., 383, 387, 433, 447
Banerji, R. C., 248, 249
Banerji, S. N., 452
Bang, S., 692, 693, 697, 700, 701
Bannister, C. O., 661
Banta, C., 481
Bar, N., 81
Barak, M., 301, 310
Barat, K., 632
Baratto, A., 710
Barbier, D., 193
Barenberg, L. H., 775
Bargellini, G., 474, 482
Barker, E. F., 194
Barker, J., 582
Barker, S. G., 633, 635, 636, 637, 642
Barker, W. F., 287, 868
Barkoff, S., 624
Barkus, O., 747, 753
Barkworth, H., 560
Barnes, B. T., 93, 110, 144, 145, 190, 738
Barnés, D., 673
Barnes, D. J., 814, 834, 835
Barnes, J., 153, 154
Barnicoat, C. R., 643
Barone, V. G., 760
Barnett, E., 504
Barr, D. P., 822
Barr, G., 608, 613, 614
Barral, P., 824
Barrat, 724
Barratt, S., 275, 368
Barrett, H. J., 584
Barritt, J., 623, 679
Barrollier, J., 73
Barsky, G., 354
Barthen, C. L., 853
Bartholomey, D. C., 772
Bartlett, J. H., Jr., 317
Barton, H. A., 325
Barton-Wright, E. C., 868
Baruishanskaya-Landsberg, F. S., 869
Barve, P. M., 390
Baryshnikova, A. N., 470
Bassett, P. R., 51, 55
Baskerville, C., 526
Baskerville, M. L., 717, 764
Bass, L. J., 518
Bass, L. W., 362, 469, 702
Basu, K., 540, 541
Basu, K. P., 213, 487, 542, 548
Basu, N. K., 854
Batchelder, E. L., 835
Bateman, J. B., 290
Bates, F., 150
Bates, F. J., 148
Bates, J. R., 125, 150, 156, 243, 245, 257, 258, 289, 302, 303, 305, 318, 319, 344, 397, 414, 529
Bates, P. M., 711
Batley, A., 345
Baudisch, O., 352, 362, 448, 449, 503, 518, 525, 882
Bauer, K. H., 411, 565
Bauer, W., 819
Baumann, C. A., 846, 853
Baumann, E., 205, 409
Baumeister, W., 254, 864
Baumgärtel, T., 720
Baumgartner, J. G., 695
Baumgartner, L., 822
Bauminger, B., 436, 449
Baur, E., 259, 339, 350, 362, 371, 441, 443, 445, 451, 512, 554, 556, 617, 856, 869, 873
Baur, W. H., 486
Bawden, F. C., 712
Baxter, J. P., 612
Baxter, R. A., 656
Baxter, W. P., 327, 328
Bay, Z., 156-158
Bayerl, V., 746
Bayle, E., 77
Bayley, P. L., 188
Bayliss, M., 51
Bayliss, N. S., 244, 291
Bayne-Jones, S., 693, 694, 698, 773
Bazuirina, E. N., 874
Bazzoni, C. B., 694
Beach, A. C. G., 381
Beard, H. H., 804
Beard, L. C., Jr., 656
Beardslee, F. C., 829
Beattie, J. M., 720
Beatty, H. A., 473
Beatty, W. A., 276
Beau, S. Le, 601
Beauverie, J., 706
Beaver, J. J., 388
Bechdel, S. I., 786, 790
Bechtel, H. E., 790, 836
Beck, A., 463
Beck, A. B., 502
Beck, H., 51, 742
Beck, H. H., 843, 844, 845
Beck, L. V., 860
Beck, W. A., 888
Becker, A. L., 36
Becker, E., 580
Becker, H., 69, 314, 330, 331
Becker, J., 562, 571, 830
Becker, J. A., 131
Becker, J. P., 672, 678
Becker, W., 612
Becking, L. B., 669
Beckley, V. A., 659
Beckman, A. O., 43, 321, 323, 333
Beckwith, T. D., 710
Becquerel, E., 6, 269, 376, 381
Bedford, C. W., 498, 527, 528, 640
Bedford, E. F., 640
Bedford, T. H., 695
Bednarczyk, W., 432
Bednyagina, N. P., 512
Beebe, M. C., 648
Beese, N. C., 149
Beesley, E., 108, 284, 287, 290
Beeson, W. M., 853
Behmel, G., 518, 521
Beil, A., 635
Bekhterev, P., 444
Beletskiĭ, F. A., 194
Bell, J., 870
Bell, L., 763
Belleaud, R. L. M., 73
Bellenot, H., 248, 254, 445, 446
Belloc, G., 790
Bellot, M., 391
Be Miller, L. N., 806
Benard, 775
Bénard, H., 688
Bender, R. C., 839, 841, 844
Bendix-Nielsen, I. B., 651
Benedict, H. C., 268
Benedict, H. M., 888
Benedict, W. L., 653, 654
Benedict, W. S., 394
Benford, F., 143, 144, 146, 190, 193, 195, 197, 198, 200, 352, 781
Bengtsson, E., 237
Benjamin, H., 822
Benjamin, M., 131
Bennekou, I., 525
Bennett, H. B., 785
Bennholdt-Thomsen, C., 759
Benoit, 5
Benrath, A., 346, 361, 396, 400, 511, 515, 529, 532, 540
Benson, G., 421
Benton, A. F., 441
Bentzen, T., 643
Benvenuto, E., 752
Benz, F., 852
Béraneck, J., 486, 538
Berchet, G. J., 411
Berczeli, H., 365
Beretta, U., 297
Berezovskaya, F. I., 454
Berg, W. F., 378
Berge, K., 444
Bergel, F., 544
von Bergen, W., 622
Berger, E., 176
Berger, G., 368, 442, 444, 451
Berger, G. W., 654
Berger, L., 438
Berger, W. E., 351
Bergfeld, W., 777
Bergmann, 23, 24
Bergmann, E., 395, 403, 671, 672
Bergmann, P., 316
Bergmann, W., 817
Bergstrom, F. W., 44, 320, 321, 349

Berke, J. D., 824
Berkey, W. E., 48
Berlemont, G., 78
Bernal, J. D., 810
Bernard, J. E., 693
Bernauer, C., 868
Bernd, E. C., 722, 829, 840
Bernhard, A., 792, 825
Bernhard, O., 769, 770, 778
Bernhardt, F., 78, 366
Bernheim, 784
Bernheim, G., 663
Bernheim, M., 780, 781
Bernoulli, A. L., 432, 433
Bernreuther, F., 287
Bernstein, G., 597, 598
Bernstein, P., 337, 425
Berry, E. R., 151
Berry, G. P., 712
Berryhill, W. R., 823
Berthelot, A., 671
Berthelot, D., 206, 274, 281, 299, 310, 318, 322, 324, 330, 351, 359, 393, 402, 406, 408, 414, 416, 418, 422, 425, 428, 432, 433, 434, 435, 437, 440, 448, 456, 457, 458, 461, 462, 463, 466, 518
Berthoud, A., 248, 254, 255, 259, 343, 344, 351, 404, 445, 446, 447, 480, 485, 486, 487, 488, 538, 541, 548, 549
Bessemans, A., 757
Besson, A., 534
Bestucheff, 360
Bethke, R. M., 787, 831, 838, 841
Betz, H., 31
Beuner, H., 793
Beunes, A., 52
Beutel, E., 589, 615, 678
Beutler, H., 265
Bevan, P. V., 282, 284
Beyersdorfer, P., 432, 434
Bhaduri, B., 516
Bhagwat, W. V., 186, 188, 280, 364, 442, 446, 538
Bhargava, L. N., 522, 883
Bhargava, P. N., 250, 440
Bhatnagar, S. S., 253, 267, 268, 358, 360, 390, 486, 698
Bhatta, B., 447
Bhattacharji, A. K., 337
Bhattacharya, A. K., 210, 250, 251, 252, 260, 344, 345, 350, 364, 369, 371, 387, 434, 446, 447, 450, 452, 541
Bhattacharya, S. C., 538, 548
Bhattacharya, S. K., 450, 486, 538
Biancani, E., 688
Biancani, H., 688
Bichowskaja, A., 776
Bichowsky, F. R., 25, 241
Bidot, E., 612
Bidwell, S., 269
Bie, 692
Bielecki, J., 401, 416, 431, 435
Bieliavski, V., 554
Bier, O. G., 863
Bierer, J. M., 607
Bierry, H., 402, 433, 434, 851, 852, 871
Biggs, G. D., 120
Bigiavi, D., 499
Bilek, F., 837
Bilham, P., 831
Billen, F., 366
Billmann, A., 517
Billon-Daguerre, A. L., 124
Bills, C. E., 716, 790-795, 797, 803, 805, 806, 807, 809, 813-817, 820, 822, 823, 828, 832
Biltz, H., 493
Bincer, H., 621
Bing, F. C., 846
Bing, K., 610
Bing, M., 722
Binkley, S. B., 856
Binks, 66
Binz, A., 400
Binz, C., 405
Biquard, D., 188, 454
Birch, S. F., 413, 656
Birch-Hirschfeld, A., 762
Bird, L. F., 80, 105, 133, 135
Birge, R. T., 163, 225, 227, 235, 282, 293, 308, 317
Bischoff, M. A., 663
Biswas, N. N., 350
Biswas, S. C., 351
Bittenbender, H. A., 175
Bjerrum, N., 218
Blacet, F. E., 419, 420, 421, 422, 424
Black, A., 780, 788, 789, 791, 830, 839, 853
Black, C. K., 385
Black, N., 727
Black, W. A., 716
Black, W. C., 824
Blackberg, S. N., 824
Blackburn, P. W., 723, 728, 729
Blackett, P. M. S., 229
Blackie, K. G., 411
Blackman, F. F., 873
Blackman, S. S., Jr., 749
Blair, G. W. S., 391
Blair, J. M., 378, 380
Blaisdell, C. A., 620
Blake, G. G., 50
Blake, G. J., 76
Blake, H. D., 143
Blake, J. T., 596
Blanc, C., 530
Blanchard, E. W., 759
Blank, I. H., 695
Blanksma, J. J., 496
Blasi, D., 775
Blegvad, O., 858
Blickensdorfer, P., 689
Bliss, A. R., Jr., 814
Bliss, H. J. W., 548
Blix, G., 822
Bloch, B. M., 429
Bloch, C. E., 751, 774, 779
Bloch, E., 7
Bloch, F., 372
Bloch, L., 7, 167
Blocher, J. M., 720
Blochinzew, D., 374
Blom, A. V., 564, 580
Blum, G., 715
Blum, H. F., 629, 760, 860, 862, 863, 864, 865, 866
Blumberger, J. S. P., 624
Blunt, K., 846
Blunt, T. P., 692
Boake, A., 545
Boardman, R., 60
Boas, 42
Bocchi, C., 362
Bock, F., 816
Bockemüller, W., 440
Bodenstein, M., 206, 207, 210, 211, 248, 251, 272, 274, 275, 276, 278, 279, 280, 281, 283, 284, 286, 287, 288, 289, 290, 297, 298, 305, 306, 307, 311, 312, 313, 314, 347, 505
Bodforss, S., 493
Bodnár, J., 868
Boehm, E., 320
Böhm, H., 297
Böhme, H., 743
Boer, A. G., 815
Boer, J. H. de, 141, 372, 374, 479, 670
Böeseken, J., 403, 404, 476, 564, 565
Böttger, O., 518
Bogdanova, G. P., 748
Bogert, M. T., 423, 491
Boggio-Lera, E., 366
Bohr, N., 17, 21, 22, 163, 214, 218
Bohstedt, G., 786
Boissonas, C. G., 524
Bokinik, Y. I., 381, 383
Bol, C., 124
Bolin, I., 449
Boll, F., 857
Boll, M., 107, 248, 369, 370, 443
Bolland, J. L., 332, 596
Bolley, D. S., 572
Boltzmann, L., 15
Bomskov, C., 754
Bonacini, C., 663
Bond, W. R., 268
Bondy, H. F., 602, 603
Bonhoeffer, K. F., 156, 214, 226, 230, 231, 242, 258, 272, 273, 275, 297, 302, 304, 317, 319, 320, 372, 393, 453
Bonner, J., 850
Bonnet, L., 346
Bonnet, R., 681
Bonsignore, A., 849
Bonsor, S., 723
Booher, J. E., 272, 537
Book, G., 544
Boone, F. H., 783-785
Booth, H., 307
Booth, H. S., 124
Booth, R. G., 817, 848
Borden Co., 842
Bordier, H., 127, 209, 293
Borgeaud, P., 812, 832
Borgwardt, E., 431, 514
Born, M., 373
Borocco, A., 367
Borrows, P. J., 776
Borsiewicz, A., 754
Borstler, E. W., 35
Boshell, G., 678
Bothamley, R. P., 355
Bott, J., 46
Bottomley, 73, 78
Bottomley, J. F., 151
Bouchard, J., 390
Boudyline, V. G., 748
Bourdillon, R. B., 798, 800, 801, 803-806, 821
Bourguel, M., 412
Bouse, V., 523
Bousquet, E. W., 548
Bousset, R., 480
Boutaric, A., 390
Bover, J. R., 386
Bovet, D., 860
Bovie, W. T., 71, 72, 77, 674, 696, 698, 716, 758, 789
Bovis, P., 275, 345
Bowden, F. P., 339, 808, 848, 849, 854, 856
Bowden, S. T., 626
Bowen, E. J., 187, 216, 246, 247, 261, 298, 307, 328, 329, 347, 348, 404, 417, 418, 422, 423, 425, 426, 428, 430, 474, 475, 477, 509
Bowen, I., 7
Boyce, J. C., 293
Boyd, H. T., 531
Boyd, M. J., 862
Boyer, J., 513
Boyle, E., 855
Brabender, C. W., 45
Brackett, 20
Brackett, F. P., Jr., 43, 104, 524
Brackett, F. S., 873
Bradford, 763
Bradshaw, E. C., 330
Bradshaw, H., 592, 609
Brady, M. J., 814, 834
Brady, O. L., 494
Braehmer, F., 292, 299

Bragg, W., 8
Bragg, J. H., 841
Bramhall, E. H., 46, 48
Branchen, L. E., 588
Brand, K., 550
Brand, T. von, 822
Brandt, A., 62
Brandt, K., 630, 686, 689, 703, 818
Branion, H. D., 814
Brannigan, P. J., 343
Braselton, C. H., 139
Bratiano, S., 822
Brattain, W. H., 93
Brauchli, E., 796, 833
Brauer, G., 346
Braun, E., 266, 432
Brauner, L., 669
Brauner, M., 669
Braunsdorf, K., 556
Brautigam, 452, 482
Bravo, G., 636, 640
Brawn, G., 758
Braz, J. le, 169
Brdicka, R., 368
Breadner, R. L., 142
Bredig, G., 64, 315, 339, 416, 449, 516
Breguet, A., 588
Bremer, K., 490
Brenard, G., 320
Brenschede, W., 313, 346, 394
Brewer, A. K., 31, 327
Brewster, C. M., 481
Brice, B. A., 240
Brickwedde, F. G., 385, 386, 793, 803
Briers, F., 254, 255, 279, 446
Brieger, G., 680
Brigando, J., 670
Briggs, G. E., 872, 875, 876
Briggs, I. A., 856
Briggs, S., 362
Brillouin, L., 374
Briner, E., 62, 533
Brings, T., 319
Brinkman, H., 52
Brintzinger, H., 679
Briot, A., 349
British Celanese, Ltd., 173, 411, 585
British Hanovia Co., Ltd., 129
British Medical Research Council, 846
British Thomson-Houston Co., Ltd., 138, 143, 146, 150
Britton, E. C., 531
Broadbent, H. S., 723
Brock, G. C., 178
Brocklesby, H. N., 574
Brockmann, H., 816, 817
Brocq-Rousseau, D., 860
Bròde, W. R., 165, 368, 373, 624, 642, 643
Brodmann, L., 282, 474
Bromley, H. A., 619
Brons, F., 308
Brooks, B. T., 527, 530, 531, 653
Brooks, L. M., 789
Brooks, S. C., 669
Brophy, J. J., 650
Brose, H., 228
Brosset, C., 367
Brotzu, G., 758
Brougher, J. C., 819
Brous, G. C., 354
Brown, A., 170, 782, 837
Brown, A. G., 307
Brown, E. B., 699, 700
Brown, F., 885, 887, 889
Brown, G., 829
Brown, H., 756
Brown, H. T., 875
Brown, H. W., 712, 731
Brown, M., 639
Brown, R. A., 645
Brown, W. B., 574
Brown, W. G., 237, 273, 275
Brown, W. H., 754
Brown, W. L., 31
Browning, C. H., 693, 694, 697, 706
Brownscombe, E. R., 209
Bruce, H. M., 801, 805, 806, 820, 821
Bruce, P. L., 596
Bruchhaus, E., 343, 369, 370
Brück, E., 746
Brückersteinkuhl, K., 571
Brückner, J., 817
Brüll, W., 359
Bruere, A. de la, 651
Bruére, S., 720
Bruhat, G., 266, 354, 450, 463
Bruijn, H. de, 254, 264, 864
Bruijnes, J., 132
Bruner, E., 621
Bruner, L., 443
Brunken, J., 812
Brunner, K., 657
Brunner, O., 857, 858
Brunschwig, R., 656
Brusilowskii, A. M., 385
Bruylants, P., 458, 550
Bruzau, Mme., 494
Bryant, W., 217
Buadze, S., 677
Buchanan, E. B., 721
Buchanan, G. H., 354
Buchwald, K. W., 803
Buda, G. de, 645
Budde, 610
Budde, E., 282
Büchi, P. F., 439, 443, 869
Bülow, M., 849
Büngeler, W., 865
Bünger, H., 836
Bugarszki, S., 538
Bugyi, B., 689
Buhtz, E., 832
Buisov, B. V., 612
Buisson, H., 5, 97, 107, 121, 192, 193, 195, 197, 198
Bulgakosa, S. P., 849
Bulich, P. K., 495
Bundesen, H. N., 170, 173, 196
Bungartz, E., 172
Bunker, J., 268, 727, 781, 835
Bunker, S. W., 660
Bunn, C. W., 404
Bunsen, R., 18, 205, 206, 271, 285
Burawoy, A., 809
Burdick Corporation, 58, 126, 127
Bureau of Standards, 165, 169, 174, 180, 189, 579, 661, 644
Burge, E. L., 685
Burge, W. E., 685, 689, 752, 763
Burger, G., 694
Burger, H. C., 96
Burgess, C. H., 285
Burgess, R., 727
Burghardt, C. A., 601
Burgher, K., 259, 260
Burk, D., 869, 883
Burke, K. A., 398
Burke, R. E., 804
Burkholder, P. R., 887
Burns, G. R., 449, 873, 876
Burns, K., 50
Burns, L., 34, 97, 111-114, 177
Burroughs, R. E., 382
Burt, J. B., 362
Burton, H. B., 784
Burton, M., 244, 438, 439, 459, 460
Buruainâ, L., 849
E. A. Busch A.-G. Optische Industrie, 167
Buschke, A., 744
Busse, A., 816
Busse, P., 808, 810, 821
Busse, W. F., 328
Bussmann, G., 740
Butaeva, F., 93
Butenandt, A., 689, 817
Butironi, C., 291
Butkov, K., 238, 342
Butler, A. M., 839
Butler, C., 509
Butler, L. W., 556
Buttolph, L. J., 66, 75, 76, 80, 85, 89-92, 117, 130-132, 143, 182, 259

Cabannes, J., 193, 297
Cadenhead, A., 391, 421
Cady, W. G., 49
Cady, W. H., 614, 635-637, 640
Cahan, M. H., 784
Calabek, J., 695
Calame, A., 743
Calcagni, G., 354, 883
Calgano, O., 815
Califano, L., 685
Callahan, M. J., 589
Callo, A., 167, 563, 663
Callow, R. K., 806, 809, 820, 821
Cambi, L., 624
Cameron, A. E., 383
Cameron, F. K., 504
Cameron, J., 708
Camp, J. P., 5
Camp, W. H., 872
Campbell, A. N., 64
Campbell, A. W., 612
Campbell, F. L., 659
Campbell, J. A., 744
Campion, J. E., 836
Campsie, H. G., 829
Camus, 775
Candler, A. C., 25
Cannon, C. Y., 835, 838
Cannon, H. J., 846
Cantieni, R., 402-404, 422, 432, 433, 440, 521
Capper, N. S., 504, 511, 854
Carbide and Carbon Chemicals Corp., 410
Carboxyhyd. A.-G., 870
Careddu, G., 754, 755
Carey-Lea, 376
Cario, G., 190, 257
Carl, 885
Carls, H., 766
Carlsohn, H., 337
Carlson, W. W., 345
Carlton, M., 299
Carmichael, E. B., 690, 718
Carnielli, P., 749
Carnot, 775
Caro, M. de, 813
Carothers, W. H., 411, 415
Carpenter, A. W., 608
Carpenter, J. A., 653
Carr, C. J., 658
Carr, E. P., 394, 413
Carr, F. H., 539
Carrick, C. W., 814
Carrico, J. L., 401, 535
Carroll, B. H., 627
Carroll, M. J., 708
Carruthers, J. E., 422
Carst, A., 156
Carter, C. W., 863
Carter, H. D., 64
Carter, H. E., 541
Cartland, G. F., 822
Cartledge, G. H., 444, 445
Cartwright, C. H., 96, 466
Carvalho, A. P. de, 268, 493, 521
Carver, W. L., 613
Carwile, L., 326
Casparis, H., 783

Casperson, T., 704
Cass, O. W., 534
Cassel, H. W., 452
Cassidy, H., 828
Castagna, S., 756
Castelain, L., 722
Castellini, P., 849
Castiglioni, A., 468, 511, 521, 623
Castille, A., 394, 401, 458, 504, 506, 798
Castle, D. C., 854
Catel, W., 782
Cathala, J., 285, 286, 288, 311, 313
Caujolle, F., 523
Caylor, H. P., 861
Cazzini, U., 679
Cecelsky, J., 504
Cekada, E. B., 684
Celluloid Corporation, 173
Cernovodeanu, P., 693, 720
Ceruti, G., 752
Chabre, P., 853
Chacrabarti, S. N., 559
Chadwick, S., 69, 292, 293, 307
Chakravarti, D. N., 629
Chakravarti, G. C., 624
Chakravorty, P. N., 851
Chakravorti, S. K., 236
Chakroborti, B., 239
Chalkley, L., Jr., 268
Chalmers, W., 584
Chalonge, D., 156, 157, 163, 193, 297
Champion, C. H., 51
Champion, C. H., and Co., Ltd., 51
Chance Bros. & Co., Ltd., 164, 167, 169
Chance, W. H. S., 164
Chaney, N. K., 52, 829
Chapman, A. G., 872
Chapman, A. T., 532
Chapman, D. L., 69, 253-255, 279, 285, 288, 289, 292, 293, 307, 311, 446
Chapman, J., 776
Chapman, M. C. C., 287
de Chardonnet, 762
Charlampowiczowna, B., 501
Charlton, F. B., 714, 890
Chase, A. M., 857, 859
Chassard, 784
Chastaing, P., 255, 360
Chattaway, F. D., 474, 497
Chatterjee, H. K., 485
Chatterji, A. C., 377
Chatwin, J. E., 404
Chaux, R., 511
Cheesman, G. H., 332
Chemische Fabrik Buckau, 611
Chen, Y. H., 817
Cherduintzev, S., 383
Cherrington, V. A., 777
Cherry-Burrell Corporation, 844
Chertoff, G. J., 610
Chesley, A. L., 660
Chesney, J. W. D., 58, 81, 828, 840
Chesnokov, V., 874
Cheung, W. M., 348
Chevallier, A., 689, 853, 855, 856
Cheymol, J., 754
Chichester, D. F., 856
Chick, H., 789, 836
Chieffi, G., 477
Chik, W., 414
Child, R., 493
Chilowsky, C., 105
Chin, T. L., 860
Chinchin, I., 586, 619
Chisholm, C., 785
Chmura, T., 357
Chocetta, A., 863
Choron, Y., 853, 855
Chorozak, T., 742
Choucroun, N., 631
Choudhri, R. S., 887
Choun, C. K., 825
Chovin, P., 510
Chow, B. F., 865
Chow, T.-C., 330
Chretien, A., 370
Christen, C., 684
Christian, W., 687, 688, 853
Christiansen, J. A., 276
Christison, F., 34, 143, 194-197
Christy, A., 329
Chu, T. C., 414
Church, A. E., 855
Church, H. F., 608
Ciamician, G., 393, 449, 468, 470, 474, 476, 491, 493, 496, 511, 515, 517
Ciechomski, L., 294
Ciusa, R., 494
Ciusa, W., 555
Claflin, D., 819
Claman, I., 819
Clar, E., 504-506, 511
Clark, A. B., 858
Clark, G. L., 43, 209, 572, 593, 663
Clark, J., 104, 170, 675, 733, 740, 748, 775, 784
Clark, L. H., 111, 798
Clark, W., 379
Clark, W. M., 621
Clarke, H. T., 183
Claude, A., 36
Claude, G., 142
Claus, W. D., 707, 768
Clausen, S. W., 825
Clément, L., 463
Clewell, J. H., Jr., 591
Clifton, C. E., 860
Cline, J. E., 330
Clover, G. R., 586
Clusius, K., 332
Cluzet, J., 391, 756, 885
Coade, E. N., 170, 173, 196
Coblentz, W. W., 34, 50, 57, 96, 97, 99, 106, 107, 109, 127, 128, 144, 146, 147, 165, 166, 174, 175, 183, 188, 194, 195, 198, 200, 201, 377, 694, 695, 711, 738
Cochran, R. L., 175
Coe, M. R., 560, 561, 611
Coe, W. S., 209
Cochn, A., 69, 182, 246, 253, 272, 274, 275, 281, 286, 299, 308, 314, 318, 330, 331, 339, 529
Cofman, V., 592
Cohen, F. H., 852
Cohen, J., 772
Cohen, W. D., 403, 404, 476, 477
Cohn, B. N. E., 818
Cohn, C., 670
Cohn, W. M., 35, 156
Colange, G., 295
Colby, W. F., 227
Cole, A. F. W., 283
Cole, V. V., 822
Colebrook, D., 776
Colebrook, L., 775, 776
Colefax, M. A., 173
Coleman, C. H., 531
Coleman, J. J., 380
Colgate-Palmolive-Peet Co., 743
Colla, S., 888, 890
Collazo, J. A., 822
Collens, W. S., 774
Collier, H. B., 680, 683, 684
Collin, A., 476
Collinet, M., 273
Collins, H., 691
Collip, J. B., 819
Colman, H. C., 816
Colthoff, P. J. G., 411
Coltman, R. W., 51
Columbo, G., 621
Comel, M., 819, 824
Committee on Photochemistry, National Research Council, 96
Common, R. H., 819
Compagnie des Lampes, 142, 179
Compagnie Lorraine de Charbons pour l'Electricité, 51
Comptoir des textiles artificiel, 617
Compton, A. H., 8, 9, 25
Compton, K. T., 31, 47-49, 81-83, 93
Conant, J. B., 421, 489, 878
Condon, E. U., 163, 235
Condorelli, F., 861
Cone, L. H., 626
Conklin, E. P., 545
Conner, H. W., 890
Connerade, E., 478, 547
Conrad-Billroth, H., 271, 416, 467, 469, 479
Conradty, E., 58
Conradty, O., 58
Consortium für Elektrochemische Industrie, 422
Continental Caoutchouc and Gutta-Percha Co., 652
Cook, A. H., 500
Cook, G. A., 305, 344
Cook, J. W., 504
Coolhaas, C., 710
Coolidge, W. D., 803
Cooper, 773
Cooper, C. A., 81
Cooper-Hewitt, P., 66, 76, 77
Cooper-Hewitt Electric Co., 72, 80, 650
(see also General Electric Vapor Lamp Co.)
Coper, K., 383
Corbet, A. S., 350, 351
Corbière, J., 271, 326
Cordes, H., 275, 282, 330, 529,
Correa, L., 669, 803
Cornbleet, T., 742, 849
Cornelius, F., 293
Cornil, L., 689
Corning Glass Works, 142, 165, 169, 172, 173
Cornu, M. A., 7, 78, 192, 195
Cornubert, R., 516
Corson, W. C., 825
Cortese, D., 555
Cossu, F., 676
Costa, R. M. da, 491
Coster, D., 308, 447
Coster, J. H., 831
Cotton, A., 266, 383
Coulon, A. de, 766
Coulsen, E. A., 489
Coulter, C. R., 670
Coulter, J. S., 770
Coulter, M. D., 724
Council of Physical Therapy, American Medical Association, 769
Courmont, J., 127
Courtman, H. R., 515
Cousin, E., 683
Coward, K. H., 789, 790, 791, 802, 817, 819, 837, 853
Cowdry, E. V., 822
Cowen, R., 846
Cowper, W., 647
Cox, G. L., 772
Cox, S. J., 853
Cox, W. M., Jr., 797, 803, 805
Craciunescu, E., 472
Craggs, H. C., 288, 289, 291
Craig, F. N., 882
Craig, J. D., 834
Craig, P., 146
Cramer, F., 279

Cramer, H., 741
Cramer, W., 748
Crary, R. W., 401
Cravath, A. M., 83
Creach, P., 683
Creamery Package Manufacturing Co., 844
Creighton, H. M., 722, 829, 840
Cremer, E., 288, 298, 302
Cremer, W., 687
Crespi, E., 633
Crespi, M., 310
Crew, H., 3, 49
Crew, W. H., 94, 95, 109
Crews, S. K., 853
Crichton, J. A., 786
Cricks, Rigby and Rigby, Ltd., 60
Crimm, P. D., 818, 823, 824
Crist, J. W., 848
Crist, R. H., 121, 122, 170, 172, 344, 357, 358, 881
Croad, A. K., 100, 105
Crockford, H. D., 354
Crofts, E., 744, 745
Croll, P. R., 586
Crone, H. G., 425-427, 430, 431
Cronheim, G., 742
Crook, W. J., 662
Crookes, W., 164
Cropp, W., 367
Cross, C. L., 176
Crowe, M. O'L., 690
Crowfoot, D., 810
Croxatio, H., 819
Croze, A. B., 723
Crozier, R. N., 411
Cruikshank, W., 284
Crumpler, C. J., 461
Cuccudoro, M., 651
Cultrera, R., 353, 849
Cumming, W. M., 493, 499, 503
Cunliffe, P. W., 128, 346, 615, 623, 633, 636, 638
Cunningham, E. L., 657
Cunningham, G. L., 441
Cunningham, H. L., 853
Cunningham, I. J., 818
Cunningham, J. P., 464
Cuny, L., 832, 840
Curie, M., 708
Curme, G. O., Jr., 411
Curry, J., 882
Curtis, H. A., 340, 345, 634
Custis, H. H., 471, 522, 540, 553
Custers, J. F. H., 479, 495, 670
Cuzin, J., 860

Dacheux, P., 656
Dachlauer, K., 532
Dadieu, A., 224
Dadlez, J., 293
Daehn, E., 492
Dahm, T. M., 177
Dailey, H. T., 268
Dain, B., 104, 341, 452
Dainton, F. S., 461
Daire, P., 720
Daland, G. A., 674, 716
Dale, H. H., 819, 821
Dale, M. L., 823
Dalen, G., 643
Dalmer, O., 814
Damon, G. H., 426, 427
Dana, D. W., 76, 92
Danckwortt, P., 167, 663
Dane, H. R., 885
Danelli, J. F., 811
Dangeard, P. A., 871, 888
Daniels, A. L., 789, 830
Daniels, F., 122, 190, 209, 210, 326-328, 426, 427, 486, 535, 802-804, 813, 876
Danilov, A. N., 873
Dann, A. T., 489
Dann, W. J., 555, 854
Dannmeyer, F., 846
Darrow, K. K., 40, 47
Dartnall, H. J. A., 857
Darwin, C. G., 17
Das, N., 689
Dastur, N. M., 856
Dastur, R. H., 873, 874, 877, 882
Datta, A. K., 272, 275
Datta, S., 239
Daugherty, K., 716
Daure, P., 275
Dauvillier, A., 193, 209
Davey, W. P., 591
David, W. T., 209
Davidovitch, P., 168
Davidshöfer, F., 877
Davidson, D., 518
Davidson, D. L., 823
Davidson, J. G., 579
Davies, A. C., 156
Davies, D. R., 821
Davies, E. C. H., 391
Davies, J. B., 869
Davies, J. S. H., 549
Davies, L., 139
Davies, W., 476, 489
Davies, W. L., 561
Davis, C. C., 607
Davis, G. E., 750
Davis, L., 711, 726
Davis, M. E., 691
Davis, N. W., 293
Davis, R. F., 655
Davis, T. L., 266
Davis, T. W., 459, 460
Davis, W. S., 721
Davisson, C., 11
Davy, H., 50, 310
Davydov, B. I., 31
Dawsey, L. H., 303, 327, 339
Dawson, L. H., 94, 109, 160, 299, 338
Dawson, T. R., 610
Daynes, H. A., 608
De, N. K., 854
Deady, W. F., 638
Dean, H., 578
Dean, R. S., 524
Deb, S., 240
De Broglie, 8, 10, 26
de Bruijn, H., 254, 264, 864
Debye, P., 17
Deck, W., 271
Decourt, J., 756
Dede, L., 387
Dedichen, H., 514
Deeney, J. J., 644
De Fazi, R., 432, 477, 492, 511, 517, 710, 826, 885
Deforge, A., 651
Defries, R., 599, 605
Degea, A.-G., 165
Degkwitz, R., 821
Degos, R., 756
Deichsel, S., 659
Dejardin, G., 193
de Jonghe, A., 511
Dejust, L. H., 818, 824
Dekking, A. C. B., 474
De Kowalski, J., 41, 156
Delaplace, R., 798, 804
Delf, E. M., 715, 885
Dell Aquila, A., 755
Delore, P., 559
Demarest, B., 816
Demina, E. N., 591
Deming, L. S., 193
Demo, M., de, 516
de Moncetz, A., 209
Demoussy, E., 715, 887
Denes-Goetz, J., 793
Denham, A. F., 587, 590
Den Hoed, D., 679
Dennington, A. R., 723
Dennison, D. M., 224, 226
Denstedt, O. F., 574
Depew, H. A., 607
Deppe, M., 806, 810, 816
Deribas, D., 756
Déribéré, M., 556, 619, 620, 624, 635, 663, 665
De Rienzo, A., 819
De Right, R. E., 399, 537
Derow, M. A., 856
Derrett-Smith, D. A., 624
Desai, B. L., 877
Desai, B. N., 390
Desai, M. S., 238, 239
Desai, S. V., 350
De Sanctis, A. G., 834, 841
Desavitsch, E. C., 824
Desbaillets, J., 62
Des Bancels, J., 871
Des Bancels, L., 585
Descamps, R., 450
Deschwander, J. von, 751
Descombes, F., 727
Desha, L. J., 665
Deslandres, H., 218
Desmurs, G., 651
de Swietochowski, H., 772
Deutsch, H., 819, 822
Deutsche Gasglühlicht Auer-Ges., 172
Deutsche Spiegelglas A.-G., 166, 167, 171
De Vaney, G. M., 814
Devers, P. K., 139, 151
Dewar, J., 35, 294
Dewey, L. H., 103, 356, 364, 443
De Wolf, C. E., 885
Dey, B. B., 488, 503
Deysher, E. F., 558
Deželić, M., 872
Dhar, N. R., 188, 193, 194, 210, 247-253, 259, 260, 290, 299, 337, 344, 345, 350, 351, 357, 364, 371, 432, 434, 440, 442, 445-447, 450, 452, 522, 538, 541, 553, 559, 629, 673, 826, 867, 869, 870, 874, 883
Dhéré, C., 698
Diacono, H., 758
Di Archangel, N., 660
Dickerson, T., 387
Dickhausser, E., 411
Dickinson, R., 494
Dickinson, R. G., 43, 258, 295, 306, 319, 321, 323, 327, 328, 336, 344, 347, 363, 371, 400, 401, 446, 534-536
Dieke, G. H., 272, 416
Dieffenbacher, K., 376
Diehl, F., 759
Dienert, F., 370, 720
Dieterle, W., 183
Dietsch, W., 600
Dietz, E. M., 878
Dietzel, R., 449, 493
Digby, W. P., 580
Dillman, L. M., 432, 703, 826
Dillon-Weston, W. A. R., 711
Dilthey, W., 647
Dimroth, 808
Dimroth, K., 795, 796, 809, 810, 812
Dingee, A. L., 34
Dingle, H., 192
Dingwall, A., 495, 564
Dinjasky, K., 515
Dinsley, A., 650
Dippel, C. J., 495, 670
Di Renzo, F., 681
Disch, J., 68
Discherl, W., 421, 451, 670
Dithmar, K., 805, 807
Ditmar, R., 598-600, 610
Ditto, Inc., 645

Dittrich, E., 463
Ditz, H., 615
Ditzler Co., 587
Dixon, H. H., 872
Dixon, J. K., 317, 321
Djang, T. G., 444
Doan, F. J., 563
Doan, G., 46, 49
Dobbie, J. J., 249
Dobrokhotova, E., 865
Dobson, G. M. B., 193
Dock, E. H., 608
Dodds, E. C., 785
Dodge, J. K., 721
Doerflinger, 591
Döring, B., 873
Doering, U. W., 131
Dogadkin, B., 593, 602, 605
Dognon, A., 862
Doisy, E. A., 856
Doktorsky, A., 742
Dolk, H. E., 873
Doll, J. H., 346
Dols, M., 814
Donat, H., 472
Donat, K., 257
Doniach, I., 865
Donnan, F. G., 398
Donovick, S. E., 710
Dooley, D., 144
Doran, W., 354
Dorcas, M. J., 50, 51, 55, 57, 60, 96, 101, 659, 829, 839, 841-844
Dorée, C., 614
Dorfman, M., 520
Dorgelo, H. B., 271
Dornic, P., 720
Dorno, C., 99, 195
Dorsey, N. E., 5
Dote, S., 585
Douglas, S. D., 411
Douglass, E., 856
Doull, J. A., 775
Dove, 156
Dove, W. F., 788
Dow Chemical Co., 64, 531
Dow, O. D., 839, 846, 848
Downes, A., 692
Downes, A. C., 53, 198-200
Downs, C. R., 504
Dowsing, 66
Dozier, C. C., 188
Dozois, K. P., 704
Dragulescu, C., 467
Draisbach, F., 172
Draisbach, H., 172
Drake, T., 814, 830, 837
Draper, J., 205, 284
Dreinhöfer, R., 482
Drekter, I. J., 792
Drew, A. H., 748
Dreyer, G., 717
Dreyfus, C., 173, 592
Dreyfus, H., 411
Dreyfus-Sée, G., 761
Drigalski, W. von, 740
Drikes, O., 267
Drinker, P., 782
Drucker, P., 755
Drucker, S. V., 559
Drummond, J. C., 789-791, 816, 831, 853, 855, 856
Druyvesteyn, M. J., 131
Dry Milk Co., 840
Dryco Co., 842
Dube, H. L., 442
Dubois, R., 59, 819
Dubouloz, P., 433, 670, 742, 761, 855
Du Bridge, L. A., 269
Dubrisay, R., 354, 400
Duce, W., 679
Duclaux, 692
Duclaux, J., 194, 381, 588
Dürken, B., 765
Düsing, W., 169
Dufay, J., 193, 297
Dufestel, L. G., 762
Duffau, R., 818
Duffendack, O. S., 160, 308
Dufford, R. T., 464
Dufraisse, C., 423, 508-511, 608
Duggan, F. W., 411, 412
Duggar, B. M., 708, 714, 732, 876, 885
Duguid, J. B., 821, 822
Duhme, E., 366
Dujarric de la Rivière, R., 758
Dumas, M. J., 615
Duncan, A. B. F., 317, 322, 324, 394, 428
Duncan, C. W., 790
Duncan, D. C., 591
Duncan, J. A., 159
Dunicz, B. L., 501
Dunlop Rubber Co., Ltd., 611
Dunn, F. P., 494
Dunn, J. T., 502
Dunn, M. S., 670
Dunnicliff, H. B., 358, 445, 448
Dunning, F., 743
Du Noüy, P. L., 555
E. I. du Pont de Nemours & Co., 411, 530, 534, 548, 562, 584, 591, 834
Duquenois, P., 487
Duret, G., 722
Dureuil, E., 479, 797
Durrant, G. G., 351
Dushinskiĭ, F., 244
Dushman, S., 30, 47, 94, 131
Dutcher, R. A., 780, 791, 814
Dutheil, J., 297
Dutheil, M., 297
Dutoit, 344
Dutt, S., 497, 624, 632
Dutta, A. K., 240, 324, 330, 338, 354
Dutton, H. J., 887
Dux, W., 286, 287
Dwight, C. H., 695
Dworski, M., 706
Dwyer, C. M., 708
Dyche-Teague, F. C., 611
Dyduszynski, A., 393
Dye, J. A., 781, 787
Dye, M., 848
Dyer, F. J., 853
Dyer, J., 614
Dykstra, H. B., 408, 591
Dykstra, K., 513
Dymond, E. G., 230, 231, 272
Dyson, G., 311
Dziedzicki, N., 95
Dziewulski, H. v., 82

Earle, W. R., 750
Easley, M. A., 110, 144
Eastman Kodak Co., 369, 382, 485, 588, 592, 621
Eastwood, E., 416, 424
Eberlin, L. W., 369, 382
Eberson, 773
Eberson, F., 696
Ebert, L., 337
Eccles, J., 188
Eck, J. C., 813
Eckart, C. H., 81
Ecker, E. E., 684
Eckert, A., 467, 506
Eckert, F., 174
Eckler, C. R., 853
Eckstein, A., 779, 780
Eckstein, H. C., 676
Eddington, A. S., 191
Eddy, C. E., 662
Eddy, W. H., 839
Eder, J. M., 168, 248, 361, 365, 627, 743
Ederer, S., 753
Edge, S. R. H., 618
Edgerton, H. A., 379
Edisbury, J. R., 555, 853, 856
Edlefsen, N. E., 157, 158
Edlén, B., 7, 42
Edwards, N. J., 447
Edwards, T. G., 306
Eeckhout, J., 351
Eeklen, M. van, 852
Eerola, L. V., 849
Efimov, A., 865
Efimov, W. W., 865
Egeler, C. E., 144, 147
Eggert, J., 209, 377, 378, 381, 384, 454, 455, 544, 562, 624
Eggleton, P., 849
Egidi, E., 754
Egle, K., 888
Egloff, G., 652-654
Egyesült Izzólampa és Villamossagi, R. T., 124
Ehrenstein, P., 451
Ehrismann, O., 704
Ehrmann, K., 401, 413
Eibner, A., 384, 385, 556, 564-566, 572, 574, 581, 663
Eichelbaum, G., 688
Eichelberger, M., 745
Eichler, A., 621
Eidinow, A., 101, 102, 179, 734, 741, 775, 861
Eigenberger, E., 413
Eiman, J., 836, 842
Einstein, A., 17, 191, 207, 269, 342, 355
Eisenberg, K. B., 170
Eisenbrand, J., 271, 337, 351, 479, 658
Eisenschimmel, W., 105
Eising, E. H., 727
Eisler, M. v., 873
Eissner, W., 679
Ekeley, J. B., 481, 515
Elbe, G. v., 304, 305
Elbs, K., 357, 504
Elder, H. M., 407, 548
Eldred, B. E., 533
Eldridge, J. A., 16
Elektrizitätswerk Lonza, 591
Elenbaas, W., 84, 93, 124, 135, 149, 150, 171
Eley, D. D., 262
Elgin, J. C., 322, 323
Elhart, W., 402
Elias, O. A., 830
Eliason, R. T., 770
Ellenbogen, V., 776
Ellett, A., 150
Ellingboe, E., 492
Ellinger, F., 670, 672, 673, 740, 741
Ellinger, P., 794, 851
Ellington, E. V., 835
Elliott, A., 282
Elliott, E. L., 650
Ellis, 9
Ellis, C., 544, 549, 558, 559, 565, 568, 584-586, 588, 652, 663
Ellis, G. H., 633, 643
Ellis, J. W., 235
Ellis, M. M., 679, 689
Ellis, N. R., 787
Ellis, V. K., 429
Ellison, T. E., 504
Elm, A. C., 574
Elm's, J., 575
Elöd, E., 365
Elsner, W., 529
Elster, J., 97
Elvehjem, C. A., 784, 788, 790, 836

Emeléus, H. J., 31, 259, 317, 322, 332, 333, 358, 408, 458
Emerson, H., 805
Emerson, R., 869, 875, 881
Emerson, W. B., 165
Emmerie, A., 817, 852
Emmett, A. D., 853
Emschwiller, G., 246, 385, 396, 397, 399, 400
Ende, W., 133
Ender, F., 801, 815
Engel, A. v., 52
Engel, P., 756
Engel, P. S., 849
English, S., 169, 171
Enos, G. M., 661
Enotte, M., 834
Enselme, J., 672, 766
Enss, J., 169
Ephraim, F., 370
Eppley, M., 152
Epstein, P. S., 163
Errera, J., 412, 469
Escales, R., 471
Escombe, F., 875
Escourrou, R., 617
Essex, H., 527, 530, 531
Essig, B., 841
Essinger, R., 754
Estey, R., 366
Estler, W., 749
Etzler, D. H., 440
Eucken, A., 226, 292, 293
Euler, B. von, 792
Euler, H. von, 432, 434, 449-451, 685-687, 689, 703, 710, 792-794, 818, 822, 849, 850, 854, 856
Evans, E. B., 546
Evans, H. M., 850
Evans, J., 518
Evans, M. G., 302, 322
Evans, W. M., 437
Evers, N., 855
Everse, J. W. R., 800
Ewald, E., 772
Ewell, A. W., 724
Ewest, H., 47
Ewing, P. L., 523, 689
Ewing, W. W., 284
Eyber, G., 333
Eyer, H., 670
Eymers, J. G., 881
Eyring, H., 288, 313

Fabbriotti, G. F., 556
Faber, F., 751, 755, 774, 779
Fabisch, W., 819
Fabre, R., 77, 523, 669, 750, 790, 795, 798, 860
Fabrics Coördinating Research Committee, 643
Fabrikant, V. A., 93, 119, 147
Fabry, C., 5, 97, 107, 121, 192, 193, 195, 197, 198, 271
Fachini, S., 555
Färber, E., 489, 517
Fahrion, 573
Fairhall, L. T., 711, 754
Faila, G., 209
Fajans, K., 376, 378, 380, 381
Falk, I. S., 170, 173, 196, 751
Falkenheim, C., 779, 836
Faltin, E., 670
Faltings, K., 308
Faraday, M., 6, 206
Faraday Society, 228, 261, 262
Fardon, J. C., 708
Fargo, J. M., 786
Farkas, A., 290, 337, 338, 342, 355, 394, 750
Farkas, L., 231, 242, 259, 273, 275, 290, 301, 303, 309, 310, 317, 319, 320, 322, 337, 338, 342, 355, 402, 425, 437, 438, 451
Farmer, E. H., 566, 574
Farrow, F. D., 615
Faucon, 663
Faucon, A., 400
Favre, P. A., 284
Fay, A. C., 761
Fay, H., 440
Fazal-Ud-Din, 350, 353
Fazel, C. S., 328
Fazi, R. de, 432, 477, 492, 511, 517, 710, 826, 885
Fearon, W. R., 350
Fechner, G., 741
Federitenko, A., 294
Fedorov, B. T., 658
Fedorov, F., 318
Fedorov, F. P., 334, 465
Feher, G., 837
Feige, A., 74
Feigl, F., 519
Feist, F., 547
Feldermann, F., 742
Feldmann, P., 377
Fellenberg, T. von, 777
Fellers, R. V., 724
Fels, E., 689
Felsher, A., 818
Feraud, K., 670
Ferguson, J. B., 66
Fergusson, W. C., 304
Fernau, A., 390
Fernholz, E., 689, 807, 810
Ferrari, C. G., 723
Ferrer, J., 408
Ferri, C., 596
Ferri, U., 745, 752
Ferrier, G. S., 499, 503
Ferry, J. D., 596
Fesefeld, H., 378
Feussner, O., 42
Fialkov, Y. A., 658
Fickendey, E., 601
Fichter, F., 480
Fielding, G. H., 424
Fieser, L. F., 502, 504, 809
Fink, P., 395
Finkelnburg, W., 94, 163, 188, 236, 295, 306, 307
Finn, A., 165
Finsen, N. R., 734, 769
Fischer, A., 690
Fischer, F., 68, 69, 73, 292, 299, 819
Fischer, H., 62, 680, 871, 872
Fischer, W., 339
Fischler, F., 432
Fischmann, C., 800, 806
Fischmann, C. F., 819
Fish, E. W., 824
Fish, F., 717
Fisher, H. L., 595
Fisher, R., 712
Fishgold, H., 263, 463
Fisk, C. F., 426, 543
Fitch, A. A., 662
Fitch, J. S., 854
Fitzgerald, G. F., 6
Fix, E. L., 411
Fizeau, A. H. L., 6
Fjermeros, E., 684
Flanigan, G. E., 814, 839, 841, 844, 852
Flechsig, W., 372
Fleisch, A., 831
Fleischhauer, R., 550
Fleming, W. D., 782
Fleming, W. E., 659
Flesch, W., 864, 879
Flexser, L., 495
Flinn, F. B., 825
Florentin, D., 539
Flores, A., 703
Floresco, N., 611
Florkin, M., 685
Flory, P. J., 293, 295, 300, 325
Flynn, O. R., 129, 638, 639
Foa, P., 785
Fodor, M. E., 847
Fokeev, V. M., 661
Folger, H. T., 716
Follet, D. H., 853
Fontaine, H., 124
Fontès, G., 745
Fonteyn, M., 458
Fonzes-Diacon, 663
Foote, P. D., 190
Forbes, G. S., 43, 44, 84, 87, 88, 96, 101, 103-105, 108, 115, 119, 123, 129, 130, 182, 190, 297, 298, 330, 355, 364, 404, 418, 459, 480, 524, 536, 537, 716
Fordyce, C. R., 621
Forney, J. D., 47, 132
Forsythe, W. E., 34, 110, 143, 145, 190, 194-197, 738
Fortrat, R., 190
Fosbinder, R. J., 802, 811
Foster, D. G., 624
Foster, G. W. A., 75
Foster, M. L., 671, 673
Foster, P. C., 748
Foucault, J. B. L., 6
Foulke, T. E., 138
Found, C. G., 30, 47, 132
Fowle, F. E., 193
Fowler, A., 25, 33
Fowler, G. J., 346
Fowler, R. D., 161-163
Fowler, R. G., 64
Fowler, R. H., 17, 377
Fox, G. W., 308
Fox, J. J., 249
Fragstein, K. v., 189
France, W. G., 567
Francesconi, L., 559, 807
Francis, G. V., 869
Franck, J., 26, 34, 163, 190, 217, 229, 231, 232, 234-242, 244, 247, 257, 262, 264, 295, 302, 330, 331, 335, 337, 338, 342, 355, 357, 375, 864, 878-881
Frank, A., 416
Frank, I., 167
Franke, A., 420, 473, 869
Franke, W. K., 310, 537
Frankenburger, W., 105, 259, 301, 302, 305, 376, 378, 464, 628, 629, 732, 739-741, 833
Frankfurt, M., 633
Franklin, R., 107, 128
Franklin, R. G., 96, 382, 674
Franta, I., 596
Fraps, G. S., 350
Fraps, R. M., 832
Fraser, H. D., 79, 131, 135
Fraunhofer, J. von, 4
Fred, E. B., 831
Fredenhagen, K., 380
Frederici, 452, 482
Freedman, P., 139
Freeman, I. M., 156, 163
Freeman, S., 818
Freer, P. C., 103
French Office Nationale des Recherches et Inventiones, 607
French, C. S., 881
French, H. S., 431
Frenkel, J., 375
Frenkel-Tissot, H. C., 751
Freri, M., 517
Frerichs, M., 834
Frerichs, R., 293
Fresnel, A. J., 4
Freudenberg, K., 567, 670, 679
Freund, L., 743
Freund, M., 655, 656
Freund, R., 823

Freundlich, H., 389
Frevberg, J., 493
Frewing, J. J., 464
Frey, C. N., 709, 822, 833
Frey, F. E., 407, 656
Freytag, H., 495, 498, 518-520, 646, 651, 890
Fricke, H., 209, 402
Fridericia, L. S., 858
Fridlyanskaya, F. M., 571, 574
Friedberger, E., 725, 758
Friederich, P., 388
Friedlander, A., 748, 774
Friedman, I., 775
Frieser, H., 368
Fritsch, C., 168
Fritsche, J., 205, 504
Fritze, O., 142
Fritzsche, H., 852
Froentjes, W., 369, 464, 500
Fröhlich, H., 373
Fröhlich, W., 861
From, V. C., 832, 840
Fromageot, C., 419, 451
Fromberg, B. M., 168
Fromherz, H., 271, 338, 380, 663
Fromray Co., 828
Frontali, G., 753, 754
Frost, F. M., 765
Frühling, G., 131
Fry, H. E., 885
Fry, H. S., 361
Fry, J. D., 599
Fuchs, L., 801, 811
Fürst, R., 503
Fues, E., 373
Fugassi, P., 405
Fujii, M., 877
Fujikawa, F., 506
Fujita, H., 608
Fukumoto, Y., 163, 396, 402
Fukushima, I., 500, 572, 625
Fulchignoni, E., 691, 741
Fuller, H. J., 888, 889
Fuller, H. Q., 243
Fulmer, E. I., 709
Fulton, H. R., 694, 695, 711
Fulweiler, W. H., 153, 154
Funk, C., 780
Funkhauser, J., 624
Furniss, A., 747
Fuson, R. C., 492
Fuwa, K., 169, 172

Gabathuler, A., 836
Gabel, W., 550
Gabor, D., 58
Gabryelski, W., 432
Gacks, H., 860
Gaede, J., 805
Gaedertz, A., 764
Gaertlein, C. W., 42
Gärtner, I., 704
Gaffron, H., 261, 264, 509, 510, 863, 864, 876, 879-881
Gage, F. H., 271
Gage, H. P., 165
Galecki, A., 388
Galeotti, G., 696
Galinsky, A., 365
Gallagher, P., 268
Gallay, W., 593
Gallerani, G., 733
Gallois, J., 75
Galloway, I. A., 712, 860
Gamble, D. L., 578, 580, 585
Ganassini, D., 449, 457
Gandini, A., 550
Ganguli, P. B., 391
Ganguly, P. B., 362, 390
Ganguly, K. L., 471, 472
Gans, L. W., 670
Gant, V. A., 523
Garcia-Banús, A., 626
Gardano, G., 869
Garlner, C. E., Jr., 728
Gardner, H. A., 385, 386, 566, 569, 574, 578, 580, 581
Gardner, J. H., 507
Garner, T. L., 593, 600, 608
Garner, W. E., 210
Garot, L., 761
Garratt, A. P., 333
Garrett, M. W., 139, 366
Garrett, O. F., 723
Garrett, R. L., 860
Garrison, A. D., 385
Garrison, E. A., 818, 819
Garver, H. L., 761
Gaschler, A., 366
Gassul, 772
Gasteyer, T. H., 825
Gasul, B. M., 823
Gates, F. L., 525, 683, 696-701, 705, 706, 708, 712, 714, 755, 775, 789
Gattefossé, H. R., 743
Gatterer, A., 64
Gaudechon, H., 206, 274, 281, 299, 310, 318, 322, 324, 330, 351, 359, 393, 402, 406, 408, 414, 416, 418, 422, 425, 428, 432-435, 437, 440, 448, 456-458, 461, 462, 466, 518
Gaudenzi, A., 82
Gault, H., 532
Gauthier, G., 59
Gauvain, Sir H., 770
Gaviola, E., 251, 302
Gaw, H. Z., 717
Gay, E., 647
Gebhard, K., 636, 638
Gebhardt, K., 633
Gedda, L., 760
Gedye, G. R., 319, 321
Gee, F. H., 311
Gee, G., 408
Geffcken, H. H., 77, 139, 829, 840
Gehlen, W., 837
Gehlhoff, G., 34
Gehrke, A., 553, 559
Gehrts, A., 83, 93
Geib, K. H., 290, 317
Geigel, H., 489, 493
Geiger, G. A., 545
Geisel, W., 584
Geitel, H., 97
Gelhoff, G., 156
Gelissen, H., 723
Gell, P. V. W., 167
General Development Laboratories, Inc., 184, 828
General Electric Co., 75, 132, 142, 143, 146, 151, 169, 172
General Electric Co., Ltd., 49, 51, 142, 150
General Electric Vapor Lamp Co., 66, 80, 134-138, 259
(see also Cooper-Hewitt Electric Co.)
Genin, G., 650, 829
Gennes, L. de, 783, 784
Genthe, A., 567, 573
Genthe and Co., 514
Gentner, W., 675
George, H., 74, 77, 131
Gérard, M., 508
Gerendas, M., 271
Gericke, I., 172
Gerke, R. H., 156, 230, 272, 275
Gerlach, H., 360
Gerlach, W., 42, 662, 820
Germer, 231
Germer, E., 131
Germer, L. H., 11
Gerngross, O., 167, 563
Gersdorff, W. A., 659
Gerstenberger, H. J., 781, 783, 837, 839
Gerwe, E. G., 361
Getman, F. H., 343, 362
Getreuer, V., 702
Gex, M., 441, 451, 651, 764
Gheorghiu, C. V., 494, 495
Gheorghiu, T., 467
Ghosh, J. C., 266, 267, 361, 370, 383, 387, 418, 421, 432, 433, 440, 442, 444, 447-450, 452, 481, 484-486, 538, 540, 541, 548, 625
Ghosh, S., 369, 387
Giaume, C., 757
Giauque, W. F., 217, 227
Gibbon, P. A., 608
Gibbs, F. B., 288, 289
Gibbs, H. D., 103, 479, 480, 545
Gibbs, R. C., 25, 42, 466
Gibson, K. E., 397
Gibson, K. S., 165, 169, 179
Giemsma, G., 776
Giese, A. C., 716
Gieseler, K., 485
Gilard, P., 168
Gilbert, E. C., 363
Gildow, E. M., 777
Gill, H. A., 652
Gillam, A. E., 97, 102-104, 129, 354, 853-855
Gillard, F. W., 179
Gilles, E., 716, 885
Gilman, H., 464
Ginsburg, E., 336, 398
Ginsel, L. A., 271
Gioh, G., 670
Gioh, J., 670
Gion, L., 350
Giordani, K., 523
Giordano, G., 709
Giroud, A., 849
Gittleman, I. F., 835
Giua, 471
Giua, M., 485
Givaudon, J., 656
Givens, J. W., 670
Giza, T., 670
Glancy, A. E., 762
Glaser, F., 406
Glass, J., 754
Glass, S. W., 52
Glazebrook, H. H., 421
Glazman, S., 588
Gleu, K., 323
Glikson, E. B., 760
Glissman, A., 349
Glocker, R., 209
Glockler, G., 393
Gloor, W. E., 589
Glotz, G., 495
Glysyn Corporation, 534
Gockel, 9
Goda, S., 479
Godfrey, A. B., 788
Godnew, I. N., 217, 254
Göbel, W., 756
Gödrich, P., 661
Goehring, M., 621
Göhring, R., 288
Görne, J., 746
Göttch, O., 821
Goettsch, M., 85
Götzky, S., 209
Gohdes, W., 193
Gohn, G., 259
Goldberg, E., 206, 248, 524, 542
Goldberg, I. M., 728, 748
Goldberg, S. A., 754, 785
Goldberger, A. von, 315, 416
Goldblatt, H., 780, 789, 790, 804
Goldfinger, G., 460
Goldfinger, P., 355
Goldheim, S. L., 445
Goldschmidt, F., 366

Goldschmidt, S., 511, 567
Goldsmith, N., 479
Goldstein, A. E., 507
Goldstein, E., 292, 372
Goldstein, L., 163, 236
Goltstein, E., 75, 127, 655
Golf, A., 838
Gomberg, M., 626
Gomez-Vega, P., 860
Gonce, J. F., 775
Gonnard, 801
Gooch, M. E., 836
Goodale, H. D., 755, 787
Goodall, F. E., 829, 847
Goode, G. P., 183, 184, 828
Gooden, E. L., 659
Goodeve, C. F., 272, 275, 298, 306, 307, 329, 347, 395, 396, 461, 583, 857
Gooding, C. M., 476
Goodings, A. C., 635
Goodman, H., 743
Goodyear Tyre and Rubber Co., 599
Goos, F., 178, 432
Gorbach, G., 682, 683
Gore, V., 869, 870
Gordon, H. B., 640
Gordon, J., 757, 758
Gordon, N. E., 104, 444
Gordon, N. T., 143, 144, 193, 195, 197, 198, 200, 385
Gordon, R. B., 868
Gorin, E., 439
Gorini, P., 752
Gorkin, Z. D., 749
Goroncy, 42
Gorter, E., 846
Goshorn, J. C., 385
Goslawski, W., 479
Gottfried, S. P., 811
Gottlieb, K., 772
Gottlieb, M., 517
Goude-Axelos, J., 36
Goudsmit, S., 25, 27
Gough, J., 821
Gould, A. J., 403, 422
Gould, C. E., 167, 171
Gourdon, G., 81
Gouzon, B., 680, 851, 852, 871
Gowen, J. W., 712, 836
Goyle, D. N., 434
Grab, W., 817
Graef, F., 511
Graffe, L., 608
Graham, J. I., 329
Graham, W. P., 762
Gramont, A. de., 35
Granath, L. P., 190, 193, 293, 299
Grant, D. H., 562
Grant, J., 169, 575, 620, 663
Grant, J. H. B., 755, 789
Grant, M., 366
Grard, J., 588
Grasse, G., 651
Grassner, F., 464
Grauer, R. C., 819
Graul, O., 530
Gray, A. E., 595
Gray, E. Le B., 816
Gray, E. W., 268
Gray, G. W., 597
Gray, L. T. M., 182, 282
Gray, T. T., 624, 652
Grayzel, H. G., 774, 823
Greaves, J. E., 830
Grechanovskii, V. P., 743
Gredy, B., 412
Green, D., 775
Green, H., 597
Green, L., 875
Green, L. W., 652
Greenbank, G. R., 558, 560, 561
Greene, J., 850
Greene, M. R., 824
Greenfield, M., 773
Greenwood, G., 317
Greenwood, M., 776
Gregersen, M., 669
Gregory, R. A., 399
Greinacher, H., 35
Greider, C. E., 52, 53, 57, 115, 173, 198-200, 841
Grempe, P. M., 620
Gribov, K. A., 501
Griebel, C., 868
Griegel, C. R., 748
Griffith, H. D., 34, 51, 97, 800
Griffith, I. O., 637
Griffith, M. E., 624, 642, 643
Griffith, R. O., 228, 281, 295, 296, 341, 351, 446
Griffiths, J. G. A., 285, 304, 329, 431
Grigg, P. P., 253, 288
Grignard, V., 539
Grimes, M. A., 616
Grimm, H. G., 172
Gring, J. L., 43
Grinbaum, R., 670
Grinstein, M., 670
Grinten, L. van der, 105
Groff, F., 410
Grondall, L. O., 165
Groot, W. de, 50, 142
Gros, O., 206, 627
Gross, J., 785, 822
Grossfeld, J., 559
Grossmann, P., 431
Groth, W., 151, 295, 300, 308, 319, 393
Grotrian, W., 27, 34
Grotthuss, T. v. 205, 361
Gruhl, A., 464
Grumbach, A., 503
Grumez, M., 494
Grün, L., 624
Grüninger, W., 824
Grunder, A., 581
Grundmann, C., 425, 484
Grundmann, W., 810, 811
Grundy, J. G., 644
Grunert, K., 720
Grunfeld, M., 458
Grünfeld, O., 598, 599
Grüss, H., 532
Gudden, B., 372
Gübitz, O., 467
Günther, E., 680
Günther, G., 685, 831
Günther, P., 9, 209
Güntherschulze, A., 31, 82-84, 93
Guerrant, N. B., 850
Guerrini, G., 709, 711 861, 865
Gueurden, J., 458
Guha, A. C., 352
Guha, B. C., 689, 850, 851
Guilbert, G. D., 823
Guillaume, 5
Guillaume, A., 436
Guillaumin, C., 783, 784
Guillien, R., 294
Guillot, J., 855
Guiteras, A., 809
Gull, H. C., 271
Gulland, J. M., 484
Gunderson, F. L., 836
Gunjikar, L. K., 882
Gunn, F. D., 748
Gunther, E. R., 790
Gunther, L., 745, 754
Gunz, A., 517
Gupta, A. W., 267
Gupta, D. N. Das, 485
Gupta, P. K., 354
Gupta, R. S., 253, 486
Gurney, R. W., 374, 376, 379
Gurwitsch, L., 767
Gustavson, R. G., 813
Gutfeld, F. V., 704
Guthmann, H., 674
Guthrie, E. S., 848
Gutman, M. B., 779
Guttman, S. A., 761
Guyer, A., 410
Guyot, M., 663
Guyot, R., 479
Guzzi, A., 504
Gvozdover, S. D., 31, 82, 94
Gyemant, A., 100, 105
György, P., 754, 772, 821, 827, 850, 851
Gyulai, Z., 372

Haack, E., 504
Haas, A. R. S., 872
Haas, E., 684, 687, 688
Haas, H. E., 255
Haas, R., 670, 674
de Haas, W. J., 336, 624
Haase, E., 658
Haase, W., 366
Haber, F., 259, 302-304, 309, 317, 337, 338, 342, 355-357, 366
Haber, P., 690, 759
Haberlandt, L., 761
Hachkowskii, V., 263
Hackl, J., 633
Hadden, R., 169
Haddock, L. A., 689
Hadfield, I. H., 614, 642
Hadler, B. C., 531
Hägglund, E., 617
Haendel, W., 645
Haenny, Ch., 354
Haerdi, W., 541
Häussler, E. P., 796
Haffner, F., 789
Hagenbach, A., 47, 48
Haggie, R., 266
Hague, J. M., 109
Hahn, D. A., 518
Hahn, G., 522
Haig, C., 857, 859
Haim, 691
Haines, R. B., 722
Haitinger, M., 556, 663, 665
Halban, H. von, 271, 282, 337, 351, 437, 479, 489, 493
Halden, W., 817
Halderson, H., 824
Halford, J. O., 626
Hall, B. J., 60
Hall, G. E., 814
Hall, H., 816
Hall, P., 837
Hall, R. A., 743
Hall, R. O., 640
Hall, V. C., 271
Hallauer, C., 712
Haller, R., 617, 626, 633
Hallett, R. L., 582
Halliday, N., 850
Hallwachs, W., 107, 193, 269
Halnan, E. T., 711
Halpin, J. G., 814
Halse, O. M., 514
Halvorson, H. A., 814
Ham, A. W., 822, 824
Hamada, H., 95
Haman, R. W., 801, 815, 829, 840
Hamburger, L., 85, 380
Hamburger, T., 644
Hamilton, C. S., 549
Hamister, V. C., 52
Hammarsten, E., 704
Hammarsten, H., 704
Hammerich, T., 684, 686
Hammett, L. P., 495
Hammick, D. L., 461
Hampel, J., 506
Hampton, W. M., 164, 167, 171
Hanau Quarzlampen A.-G., 81, 132, 176
Hand, D. B., 685, 848

Hand, I. F., 200
Handley, F. W., 500
Handovsky, H., 825
Hanford, Z. M., 844, 852
Hanke, M. E., 781
Hannerz, E., 439
Hanovia Chemical and Manufacturing Co., 74, 78, 80, 100, 126, 134, 135, 137, 138, 161, 844-846
Hansen, A. M., 818
Hansen, H. C., 777
Hansen, H. V., 587
Hansen, T., 775
Hansen-Schmidt, E., 536, 548
Hanschke, G., 530
Hanson, E. A., 881
Hantzsch, A., 337, 343, 352, 368, 437
Hanyu, T., 584
Hanzal, R. F., 823
Hanzawa, T., 369
Haq, M., 522
Harada, T., 124, 366
Harai, K., 337
Harden, A., 311
Harder, R., 873
Harding, R., 139
Hardy, M., 747, 748, 775, 776
Hare, A., 51
Hare, D., 887
Haring, R. C., 365
Harkins, W. D., 36, 366
Harms, J., 464
Harmsma, A., 525
Harpuder, K., 742
Harries, W., 68
Harrington, E. A., 271
Harrington, E. L., 119, 120
Harris, D. T., 97, 116, 173, 670, 673, 678, 744, 749
Harris, E., 617
Harris, F. I., 670, 696, 716
Harris, L., 105, 283, 326, 395, 401, 437, 466, 627, 628, 818
Harris, L. J., 821. 822, 849
Harris, M., 621, 623
Harris, N. L., 74
Harris, R. S., 727, 781, 835
Harrison, 66
Harrison, D. C., 795
Harrison, D. N., 193
Harrison, G. B., 377, 379
Harrison, G. R., 87, 88, 108, 116, 119, 120, 123, 129, 130, 271, 381
Harrison, H. A., 644
Harrison, W., 142, 633, 635, 638
Hart, D., 728, 729
Hart, E. B., 784-786, 790, 836, 837, 839
Hart, E. J., 402, 543
Hart, L. P., 581
Hart, M. C., 805
Harteck, P., 151, 193, 214, 226, 259, 290, 297, 300, 303, 307-309, 317, 320, 372, 453
Hartleb, O., 390, 437
Hartley, G. S., 500
Hartley, H., 474
Hartley, J. G., 856
Hartley, W. N., 35, 40, 193
Hartline, H. K., 857
Hartman, J. I., 783
Hartmann, J., 182, 766
Hartung, E. J., 376
Harvey, A., 271
Harvey, C. E., 588
Harvey, E. H., 513, 555
Harvey, E. N., 876
Hashizuma, S., 358
Haslewood, G., 809, 816
Hashmi, M. S., 268
Hass, H. B., 526
Hasse, T., 169
Hasselbalch, K. A., 735, 736, 746
Hassko, S., 759
Hatano, T., 759
Hatch, L. F., 526
Hathaway, M. L., 815, 824
Hatschek, E., 391
Haubold, H., 823, 824
Hauch, J. T., 781
Hauge, S. M., 814
Hauptmann, H., 807
Hauser, E. A., 601
Hausmann, W., 188, 690, 750, 860, 861
Hauss, H., 432
Haussen, I., 891
Hausser, K. W., 101, 737-739
Hautot, A., 168
Haverstick, E. J., 48
Hawk, P. B., 855
Hawkins, J. A., 210
Hawkins, N. C., 823
Hayashi, M., 506
Hayashi, S., 683
Hays, M. B., 275
Hazen, H. H., 743
Heath, R. F., 720
Heathcote, R., 60
Hebb, T., 82
Heber, C. F., 743
Hecht, K., 379
Hecht, O., 408
Hecht, S., 857, 859
Heck, L. L., 464
Hedges, J. J., 636
Hedwall, I. A., 259
Heel, A. C. S. van, 238, 370
Heermann, P., 613, 622, 643
Heidt, L. J., 102-104, 122, 190, 297, 298, 340, 459, 524, 670
Heilbron, I. M., 489-491, 493, 494, 794-797, 804, 805, 809, 810, 832, 853-855, 868, 876, 882
Heilbrunn, L. V., 716
Heimann, G., 818
Heinemann, A., 415
Heinemann, F., 827
Heinish, O., 885
Heinrich, F., 333
Heisenberg, W., 10, 26, 226, 236, 243
Heitler, W., 163, 236, 237
Heitz, W., 478
Helbronner, A., 77, 78, 597, 660, 720, 721
Helferich, B., 680
Helfrich, F., 331
Heller, V. G., 848, 849
Heller, W., 391
Hellström, H., 630, 685, 686, 703, 856
Helman, F. D., 791, 794
Helmer, A. C., 847
Hemptinne, M. de, 472
Hemsalech, 35, 40, 41
Henderson, J. M., 754, 784, 786
Hendrichs, W. A., 788
Henk, H. J., 617, 624
Henkin, H., 438
Henne, A., 412, 663
Henning, F., 74
Henri, Mme., 696, 767
Henri, V., 45, 77, 78, 153, 206, 212, 213, 241, 244, 271, 314, 326, 327, 330, 339, 394, 401-403, 412, 416, 419, 425, 431, 433, 434, 451, 458, 466, 467, 469, 521, 597, 601, 610, 660, 671, 692, 693, 696, 698, 720, 721, 737, 767
Henrici, A., 396
Henriques, F. C., Jr., 324
Henriquez, P. C., 629
Henry, D. E., 98
Henry, J., 1
Henry, K. M., 836
Henry, L., 160, 324
Hensel, A., 478, 485, 490
Henszey, R. O., 840
Hentschel, H., 439
Henze, M., 522
Heraeus, 42, 68, 72, 74, 75, 151
Herber, E. K., 890
Herberg, E., 661
Herbert, R. W., 849
Herbsman, A. M., 657
Herchefinkel, H., 310
Herčik, F., 698
Heringa, G., 754
Herman, N. B., 775
Hermann, A., 244
Hermann, P., 599
Herms, W. B., 765
Herold, W., 416, 425, 437, 467
Herr, W. N., 439
Herrle, K., 680
Herrick, J. F., 512
Hershberg, E. B., 504
Herschel, J., 18, 380
Herschel, W., 6
Hertel, E., 248, 288, 290, 291, 400, 529, 532, 540, 697, 717
Herter, M., 384
Hertsriken, S. D., 172
Hertwig, 861
Hertz, H., 6, 26, 269
Herwerden, M. A. van, 766
Herzberg, G., 25, 163, 219, 228, 237, 240, 242-244, 293, 294, 326, 395, 396, 401, 414, 416, 417, 419, 458
Herzberg, K., 712
Herzenberg, H., 820
Herzenstein, A., 626
Herzfeld, K. F., 247, 276, 880
Herzog, H., 411, 658
Herzog, R., 617
Hess, A. F., 773, 778-781, 783, 785, 788, 789, 791-795, 803, 813, 814, 819, 820, 822, 825, 827, 835, 836, 838, 839, 842
Hess, J. H., 823
Hess, K., 621
Hess, W., 432, 434
Hesse, H., 825
Hessler, M. C., 780
Hessling, G. von. 464
Heubner, W., 834
Heudebert, 797
Heuer, G., 757, 758
Heurlinger, T., 220, 225
Heuvel, F. A., van den, 566
Hewittic Electric Co., Ltd., 179
Hewitt, J., 624
Heyde, V., 532
Heyl, C., 650
Heyl, F. W., 805, 822, 853
Heymann, W., 819, 822
Heymer, G., 253, 286
Heyne, G., 64, 171, 592
Heyroth, F. F., 698, 699, 701, 703, 850, 851
Hibben, H. G., 98, 99
Hibben, J. H., 224, 360
Hibben, S. G., 142, 201, 723, 728, 729
Hibbert, E., 508, 616, 633-635
Hicks, 23
Hicks, C. S., 670
Hicks, J. F. G., 619
Hickman, J. O., 829, 832, 841, 855
Hickman, K. C. D., 816
Hickman, N. V., 841
Hickson, E. F., 579, 581
Hida, T., 630
Hieger, I., 804
Higgins, G. M., 766, 788, 885
Higgins, J. A., 523, 689
Hilbert, G. E., 602
Hildebrand, C. J., 823
Hilferding, K., 279
Hilgendorf, H. J., 322, 456

Hilger, Adam, Ltd., 161, 270
Hill, D. G., 400, 406
Hill, G. A., 538, 539
Hill, G. L., 195
Hill, J. H., 658
Hill, J. W., 391
Hill, K., 680
Hill, L., 102, 636, 640, 741, 760, 775, 776, 788
Hill, O. J., 786, 790
Hill, R. A., 330
Hiller, K., 226
Hiller, W., 384
Hillstrom, H. T., 803
Hilmer, A., 617
Hilpert, S., 472
Hilsch, R., 372, 375, 378, 379
Himmelbauer & Co., 610
Hinrichs, M., 717, 763-765, 767, 865
Hinsberg, K., 553
Hinshaw, W. R., 854
Hinshelwood, C. N., 298, 318, 332, 422
Hinterberger, H., 421
Hintz, E., 650
Hippel, A. v., 68
Hiraoka, T., 169
Hirsch, A., 864, 877
Hirsch, P., 727
Hirsch, W., 804
Hirsch-Kauffmann, H., 785
Hirschberg, Y., 402, 403, 425, 671, 672
Hirschkind, W., 618
Hirschlaff, E., 273
Hirschlaff, E. N., 461
Hirschler, L., 624
Hirsekorn, H. G., 183
Hirst, E. L., 849
Hirst, H. R., 188, 633, 635-637, 642, 645
Hirst, H. S., 258
Hittorf, J. W., 36
Hixson, O. F., 846
Hlučka, F., 519
Hoar, S. B., 829
Hobert, H., 748
Hoch, H., 402
Hoch, J., 453
Hochenbichler, A., 774
Hochheim, E., 640
Hodes, H. L., 822
Hodges, F. W., 497
Hodgson, H., 474, 479, 500, 624, 643
Hoeber, R., 753
Hoefelmayr, K., 841
Hoek, C. T. van, 582
Hoeman, E. C., 653
Hönigschmid, O., 366
Hörmann, H., 52
Hövelborn, C., 741, 752
Hoffert, W. H., 656
Hoffman, 840
Hoffman, J., 173
Hoffman, La Roche, Inc., 833
Hoffman, R. M., 122, 515, 804
Hoffmann, A., 518
Hoffmann, F., 35, 124, 440
Hoffmann, J., 169, 176, 360
Hoffmann, K., 68
Hoffmann, R., 347, 348
Hoffmeister, A., 676
Hogan, A. G., 850
Hogewind, F., 513
Hogness, T. R., 231, 271, 456
Hogue, J. M., 99, 738
Hokl, J., 556
Holborn, L., 74
Holden, H. F., 670
Holden, M., 712
Holdt, P. C., 385, 386
Hole, K. W., 59
Holiday, E. R., 271, 670, 698, 851
Holladay, L. L., 179, 181, 196, 583, 738
Hollaender, A., 224, 322, 351, 707, 708, 714, 768, 776
Holley, C. E., Jr., 572
Holm, E., 858
Holm, G. E., 558, 560, 561
Holm, R., 825
Holmes, A. D., 174, 789, 813, 834, 853, 854
Holmes, E. O., Jr., 462, 634
Holmes, H. H., 327, 328
Holmes, M., 351, 358
Holmes, W., 624
Holmes, W. C., 443
Holophane Co., 147
Holst, G., 189, 630
Holt, L. E., Jr., 784, 785
Holtz, F., 796, 801, 821, 822
Holtz, P., 433, 672, 673, 751, 849
Holtzclaw, J. B., 655
Holtzmann, 124
Holweck, F., 8, 9, 708
Honeywell, E. M., 792, 795, 797, 803, 813
Hood, H. P., 169, 173
Hood, N. R., 869
Hooker, S. C., 502
Hooper, C. W., 833
Hoover, S. R., 883
Hoover, W. H., 873
Hopfield, J. J., 7, 272, 293, 308, 317, 325, 414
Hopkins, F. G., 848
Hopper, K. B., 820
Hoppert, C. A., 790, 836, 839
Hopwood, F. L., 556, 708
Horclois, R., 510
Horesh, A. J., 781, 837, 839
Horiba, S., 389
Horii, I., 683
Horio, M., 467, 495, 500, 553, 558, 572, 625
Hormuth, R., 879
Horn, V., 786
Horowitz-Vlasova, L. M., 560, 573
Horton, A. T., 428, 430
Horton, F., 156
Hoskins, W., 765
Hottinger, A., 792, 793, 818, 848
Hou, H.-C., 787
Houben, J., 339
Houck, R. C., 679
Houghton, E. M., 711, 726
Houpillart, J., 509
Householder, H., 818
Houseman, P. A., 703
Houtermans, F. G., 136
Houwink, R., 584
How, T. G., 853
Howard A., 489
Howard, C. H., 175, 787
Howard, L. B., 602
Howard, M., 754
Howe, H. E., 153
Howe, J. P., 394, 428
Howe, M. G., 754
Howell, O. R., 314, 368
Howell, W. H., 678, 860
Howitt, F. O., 676
Howland, J., 783, 784
Hoyer, D. G., 659
Hoyt, H. S., 670, 696, 716
Hubert, B., 872
Hubert, R., 755
Hudson, D. P., 882
Hudson, F. L., 412, 453, 454
Hudson, H. E., 493
Hünecke, H., 437, 674
Hüniger, M., 169
Hüttig, G., 343
Huezel, P., 620
Huffman, C. F., 790
Hughes, A. L., 109, 269, 375
Hughes, B., 400
Hughes, C. W., 50, 57, 96
Hughes, D. M., 674, 696, 716
Hughes, J. S., 143, 787, 788, 854
Hughes, W. A., 650
Huish, D. M., 493
Hukumoto, Y., 395
Hulburt, E. O., 34, 72, 75, 106, 299, 338
Huldschinsky, K., 778, 781
Hulett, M., 76
Hull, A. W., 132
Hull, F. A., 42
Hull, H., 814
Hulthén, E., 237
Hulubei, H., 95
Hume, E. M., 779, 780, 788, 789, 792, 795, 817, 847
Humiston, B., 317
Hummel, C., 142
Humphrey, G. C., 836, 837
Hund, F., 225, 226, 228
Hund, W. J., 656
Hunter, A. S., 562
Hunter, J. A., 615
Hunter, J. E., 814, 850
Hunter, V., 689
Huppert, P., 172, 176
Hurst, D. G., 161
Husa, W. J., 657
Hussey, R., 681, 683
Hutchinson, A. H., 682, 711, 716
Hutchinson, W. K., 318
Hutton, R. S., 151
Huygens, C., 3
Hyatt, J. M., 504
Hyde, 775
Hylleraas, E., 236
Hymas, F. C., 104, 353, 400
Hynek, L., 837

Iana, I., 754
Iancou, A., 754
Ibakh, B., 151
Ichikawa, T., 286
Iddings, C., 425
I. G. Farbenindustrie, A.-G., 51, 142, 172, 176, 259, 381, 395, 411, 439, 464, 532, 534, 547, 549, 562, 621, 657, 743, 821, 832-834
Iguchi, K., 836
Iimori, S., 106, 640
Ijboldina, C., 591
Ikebaka, T., 742
Il'ina, Z. A., 381
Il'ina-Bagdasar'yan, Z. A., 381
Iljina, A. A., 444
Illarionov, V. V., 653
Illuminating Engineering Society, Subcommittee on Measurement of Ultraviolet Radiation, 99
Imanishi, M., 322
Imboden, M., 816
Inaba, T., 573
Inagaki, T., 165
Indovina, R., 646, 647
Inhoffen, H. H., 807
Inman, G. E., 135, 141, 142, 146
Inman, O. L., 874
Innes, J., 821
Inoue, T., 337
Insko, W. M., Jr., 786
Ionescu, A., 326
Ionnides, Z. M., 861
Iredale, T., 280, 306, 395, 397
Irish, F. W., 853
Irlin, A. L., 657
Irvine, J. C., 869
Irving, F., 494
Irwin, G. F., 825
Isaac, E., 473
Isaachsen, H., 786

Isemura, T., 391, 436
Ishii, S., 384, 389
Issendorff, von, 82, 83, 84
Issermann, S., 743
Ito, R., 670, 685, 686, 689
Ivanova, E. N., 444
Iwamoto, K., 629

Jablczynska, H., 358
Jablczynski, K., 358
Jack, J. M., 51
Jackson, 66
Jackson, A., 368
Jackson, H., 608
Jackson, H. C., 829, 840, 841, 845
Jackson, W. F., 304, 309
Jacobi, 885
Jacobs, S., 605
Jacobson, R. A., 411, 415
Jacoby, D., 751, 752
Jacoby, G., 161
Jacqué, L., 656
Jacquemaine, R. P., 346
Jacquier, G., 359
Jaeckel, G., 168, 171
Jaeger, A. O., 481
Jaeger, C., 829
Jaeger, F. M., 368, 438, 451
Jaeger, M., 442
Jaenicke, J., 366
Jahn, F. P., 460
Jaia, F., 755
Jakobson, T., 172
Jakolewa, A., 296
Jakowsky, J. J., 609
Jalowy, B., 744
James, E. M., 814, 834
James, R. F., 723, 729
James, T. H., 380
Jameson, C. W., 635, 661
Jander, G., 369, 464
Jansen, C. H., 847
Janssen, C., 475
Jaubert, G. F., 293
Jaulmes, C., 747
Jeans, Sir J., 16, 17, 191
Jeantet, P., 381
Jecusco, F. P., 605
Jeffreys, C. E. P., 306, 347
Jendrassik, A., 782, 805, 809, 813, 833
Jenkins, F. A., 325
Jenkins, H. G., 142
Jenkins, L. D., 586
Jenkins, R., 637, 800, 801, 805
Jenkins, S. S., 477, 547
Jennen, J., 457
Jensen, J., 562
Jemma, G., 773
Jephcott, H., 785
Jerchel, D., 767
Jermstad, A., 343
Jessel, G., 772
Jesserer, H., 674, 676
Jessionek, 769
Jessop, G., 355
Jessup, D. A., 621, 622
Jette, E., 260, 262
Jeu, K-K., 410
Jevons, W., 227
Jezewski, H., 163
Jirovec, O., 523, 676, 865, 888
Job, A., 246, 385, 396, 397
Job, P., 343
Jockersch, H., 274
Joffe, C., 627
Johansson, R., 178
John, H., 467, 468, 518, 521
John, C. O., 703
Johnson, F., 784
Johnson, F. H., 711
Johnson, J. R., 747
Johnson, L. B., 111-114, 135
Johnson, M. R., 869
Johnson, R. C., 25, 53, 228, 308
Johnson, R. M., 818
Johnson, T. B., 469, 518, 699, 700, 703
Johnston, E. H., 210, 328
Johnston, E. S., 873, 882, 887
Johnston, H., 227, 243, 307, 325, 805
Johnstone, F., 805
Jokisch, R., 447
Jolibois, P., 45
Jolley, L. J., 458
Jolly, J., 759
Joly, R., 516
Jona, A., 752
Jonas, G. B., 149, 150, 171
Jones, D. C. R., 506
Jones, E. J., 327
Jones, H. A., 659
Jones, H. I., 586
Jones, J. H., 785, 818, 819, 822
Jones, L. A., 186, 271
Jones, L. T., 397, 529
Jones, N. C., 124
Jones, P. F., 388
Jones, R. N., 810
Jones, W. J., 626
Jones, W. N., 268, 610
Jonescu, A., 414
Jonescu, M., 472
de Jong, A. W. K., 482, 483, 602
Jongbloed, J., 858
Jongh, S. E. de, 679
Jonghe, A. de, 511
Joos, G., 244
Jordan, A., 743
Jordan, D. P., 830
Jordan, P., 163
Jores, A., 690
Jorg, H., 556
Joris, G. G., 408
Jorissen, W. P., 473, 474, 513, 514
Joseph, C., 562
Josephy, B., 852, 853
Joshi, C. B., 390
Joshi, J. N., 445, 448
Joshi, N. V., 351
Josse, Z., 610, 611
Jost, W., 279, 280, 284, 542
Juday, C., 876
Jürgens, E., 167
Jung, F. T., 755
Jung, G., 246, 278, 279, 286, 371
Jungers, J. C., 320, 407, 408, 415
Junghagen, S., 687
Jungjohann, W., 131
Jusatz, H. J., 825
Just, E. E., 764
Justin-Mueller, E., 363, 364

Kabanova, E. Y., 385
Kabos, W. J., 884
Kabat, E. A., 670
Kachanova, E. E., 560
Kämmerer, H., 860
Kämmerling, I., 679
Kaertkemeyer, L., 320
Kahlenberg, O. J., 814
Kahler, H., 97, 106, 107, 128, 194, 195
Kailan, A., 343, 437, 440, 452, 458, 467, 480, 529
Kaiser, H., 32
Kakefuda, H., 851
Kalb, W. C., 51, 62
Kalle & Co., 481, 647, 648
Kalish, J., 743
Kallos-Deffner, L., 752, 758
Kallos, P., 752, 758
Kambara, S., 593, 608
Kambayashi, Y., 681
Kamenskiĭ, K. V., 885
Kamerling, H. H., 492
Kamerling, S. E., 878
Kaminsky, J., 105, 627, 628, 823
Kamm, E. D., 794, 795, 797
Kamm, O., 792
Kandler, L., 624
Kaneko, H., 622
Kangro, W., 331
Kantzer, M., 365
Kapella, Ltd., 165
Kaplan, J., 163, 242, 326, 670
Kaplan, M. Y., 588
Kaplanskaya-Raiskaya, S. I., 742
Kaplanskiĭ, S. Y., 742
Kapoor, G. P., 887
Kappanna, A. N., 267, 442
Kapur, P. L., 268
Karagunis, G., 267, 380, 558
Karev, M., 101
Karl, P., 743
Karlsson, S., 793
Karpinsky, Z., 607
Karrer, P., 849, 850, 852, 854
Karrer, S., 328
Karschulin, M., 362, 365
Karshan, M., 824
Karsten, A., 651
Kasai, E., 172
Kasai, K., 506
Kasatkin, E. V., 748
Kasheninnikova, A., 837
Kassel, L. S., 210, 217, 316, 319
Kassowitz, K., 775
Kastle, J. H., 276
Kather, E., 553, 678, 679
Kato, N., 684
Kato, S., 414, 416, 548
Katowaki, H., 172
Katschanova, E. E., 573
Katz, E., 877
Kauffmann, H., 613, 614, 616
Kauffmann, H. P., 399, 457, 536, 548, 556, 565, 567
Kaufmann, W., 172
Kaul, L., 366
Kautsky, H., 254, 262, 264, 265, 333, 864, 877, 879
Kawa, J., 32, 83, 97
Kawaguchi, S., 742
Kawakami, K., 854
Kawakami, T., 681, 753
Kawasaki, K., 506
Kayser, H. G. J., 5, 271
Keating, 66
Kedrovskiĭ, B., 751
Keenan, G. L., 383
Keeser, E., 679, 680, 688, 710, 751
Kehlen, H., 595
Keilin, D., 686
Keller, E., 491
Keller, P., 734, 738, 760
Kellermann, K., 216, 284
Kellie, A. E., 848
Kellner, B., 821
Kellner, H. M., 271
Kellner, L., 804
Kelly, A., 610
Kelly, C. B., 721
Kelly, T. D., 727, 828
Kelting, R. C., 92
Kelvin, W. T., 6, 73, 78
Kelvin Bottomley and Baird Co., Ltd., 580, 640
Kemble, E. C., 217, 225, 227
Keményffi, A. G., 805, 813
Kemmler, H., 742, 825
Kempf, R., 385, 581
Kempner, W., 710
Kemula, W., 393, 394, 414, 415, 501
Kennard, D. C., 787
Kennedy, C., 850
Kennedy, D. J., 660
Kennedy, T., 810

Hilge
Hill
Hi
P
...30, 151
...41
...J., 695, 887
...er, 583
Kestner, O., 102, 733, 744
Kewley, F. E., 139
Key, J. A., 819
Keyes, F. G., 75, 530, 720
Kharasch, M. S., 545, 548, 550, 817
Khlebnikova, L. Y., 52
Khokhlovkin, M. A., 408
Khramova, E. F., 52
Kidson, 193
Kieferle, 837
Kielwein, F., 830
Kiepenhauer, K. O., 195
Kiesewetter, M., 493
Kiess, C. C., 42
Kikuzawa, T., 817
Killian, T. J., 81, 82, 94
Killick, E. M., 789
Kilpatrick, M. L., 339
Kimball, H., 193, 200
Kimberly, A. E., 619
Kimmel, L., 823
Kimovec, D., 682
Kimura, M., 240, 273, 386
Kimura, S., 501
Kinele, H., 271
King, A. A., 400
King, A. S., 23, 26
King, A. T., 623, 645, 679
King, E. J., 814, 822
King, F. A., 580, 640
King, H., 809, 810
King, H. S., 546
King, P. E., 188
King, W. N., 549
Kinsman, S. T., 642, 643
Kinumaki, S., 534
Kippen, P. J. Zonen, 271
Kipphan, H., 720
Kirchhof, F., 593, 595, 598, 600, 604
Kirchhoff, G. R., 4, 15, 18
Kirchstein, B., 47
Kirillow, E. A., 378
Kirkbride, F. W., 416, 417, 460
Kirrmann, A., 412
Kirsch, W., 790, 836, 837, 840
Kirschstein, B., 47, 49
Kirstein, F., 725
Kirzner, N. A., 500
Kisch, 770
Kisch, E., 821, 829
Kiselev, N. M., 890
Kiss, A., 271, 328
Kistiakowsky, G. B., 102, 103, 158, 214, 248, 250, 282, 283, 286, 296, 298-301, 305, 306, 309, 311, 318-320, 328, 329, 336, 341, 344, 347, 414, 416, 430, 466
Kistner, H. E., 854
Kitagawa, K., 573
Kitahara, S., 358
Kitamura, S., 758
Kitaoka, K., 640
Kitchevatz, M., 741
Kittel, S., 751
Kiu, T., 198, 382
K. L., 606
Klason, P., 868
Klatte, F., 410, 411
Klausner-Cronheim, I., 821
Klein, A., 674
Klein, D., 814
Klein, G., 867, 868
Klein, H., 531
Klein, L., 494
Klein, O., 236, 257
Klein, R. I., 823
Klein, S. J., 824
Kleinau, W., 857
Kleiner, S., 648
Klemenc, A., 300, 394
Klemm, A., 176
Klemm, W., 373
Klemme, M. S., 515
Kler, S., 760, 765
Kletzien, S., 790, 814
Kletzien, S. W. F., 822
Klever, H. W., 406
Kline, B. E., 788
Kline, G. M., 411
Kline, O. L., 837
Kling, A., 346, 539
Klingelhöfer, W. C., Jr., 283
Klinger, H., 474, 482
Klingler, C., 671
Klingstedt, F. W., 466, 469, 495, 617
Klinkenberg, A., 651
Klinkhardt, H., 301, 302, 305
Klinkott, G., 349
Klissiunis, N., 684
Klose, A., 670
Klumb, H., 169
Klugh, A. B., 717
Klussmann, E., 686, 849, 854, 856
Kluyver, A. J., 715
Klyarfel'd, B., 94
Knandel, H. C., 814
Knapp, A. W., 100, 103, 104, 127, 817, 831
Knauss, C. A., 554, 567, 568
Knebel, E., 640
Kneer, L., 689
Knight, B., 558
Knipscheer, H. M., 471, 496, 499
Knoll, A. F., 881
Knopf, E., 266
Knorr, H. V., 271, 879
Knott, J. C., 761
Knudson, A., 781, 797, 798, 802-804, 828
Kobayashi, C., 575
Kobayashi, M., 368
Kobayashi, S., 767
Kobel, E., 82
Koblitz, W., 346, 401, 510
Koboshi, S., 825
Koch, B., 106
Koch, E. M., 784, 813, 816
Koch, F. C., 703, 813, 815, 816, 822
Koch, P. P., 376
Kocher, N. S., 592
Kodama, S., 857
Köbner, T., 852
Kögel, G., 629, 632, 662, 663, 669, 680, 857, 872, 877
Kögel, J., 475, 476
Köhler, F., 413
Köhler, L., 413
Köhler, S., 620
Köhn, M., 392
Kölsch, R., 458
Koenig, A., 319
König, E., 627
Königsberger, J., 273
Koenigsfeld, H., 774
Koeppe, H., 341, 750
Koernicke, E., 95
Köser, J., 805
Kofman, T., 391, 756, 885
Kogan, N. M., 625
Kogon, M., 454
Koh, M., 749
Kohler, E. P., 489
Kohler, W., 47
Kohlrausch, K. W. F., 224
Kohn, H., 189
Kohn, H. I., 876, 881
Kojima, K., 600, 611
Kokochashvili, V., 290
Kolbert, J. W., 129
Koldayev, B., 756
Kolesnikova, N. I., 445
Kolhörster, W., 9
Kollath, W., 669, 670
Koller, G., 521
Komarov, V. A., 411
Komnick, J., 82
Kon, S. K., 791, 802, 813, 817, 835-837, 848
Kondo, M., 685
Kondrat'ev, V., 231, 238, 239, 243, 254, 273, 296, 305, 309, 324, 325
Kondrat'eva, E., 305
Konen, H., 131
Konovalov, F., 94
Konstantinova-Shlezinger, M., 330, 331, 870
Koopman, J., 747, 748, 757
Koopmans, T., 49
Kopaczewski, W., 691, 756
Koper, K., 266
Kopfermann, H., 109
Koppelmann, F., 47
Kopsch, U., 309
Korabel'nik, R. K., 253, 341
Korda, P., 624
Kordatzki, W., 384
Kornfeld, G., 137, 216, 282, 283, 330, 331, 339, 340, 443
Kornmann, J., 756
Korotkov, K. N., 513, 514
Kortüm, G., 161, 262, 271
Kosbahn, T., 42
Koschara, W., 851
Kosche, S., 632
Kosman, A. J., 865
Kossovitch, N., 758
Kostyal, L., 756
Kotecki, A., 46
Kothari, C. J., 468, 474
Kouperman, A. B., 441
Kovach, L., Jr., 64
Kovalev, T. G., 556, 653
Kovalevskiĭ, I. I., 618
Kowalsky, J. de., 41, 156
Kozak, J., 443, 549
Kozin, N. I., 571, 574
Kozlov, P. V., 588
Kozlov, V. V., 501
Kraft, J., 370
Krahl, M., 601, 605-607
Kral, F., 743
Krall, S., 601, 609, 610
Kramer, B., 783-785, 792, 805, 822, 823, 832, 835
Kramer, M. M., 852
Krantz, J. C., Jr., 268, 481, 658
Krashennikov, F. N., 874
Krasso, H., 831
Kratinova, E. P., 837
Kratzer, A., 220, 225
Kraus, A., 589
Kraus, C. A., 71, 75
Kraus, H., 689
Krause, A. C., 858
Krauskopf, K. B., 289, 418, 448
Krauss, E., 831
Krauss, F., 343, 360, 369, 370, 444
Krauss, W. E., 838, 841
Krausz, G., 364
Krauz, C., 472, 596
Kraybill, H. R., 855
Krebs, H. A., 749
Krefft, H., 97, 115
Kreibich, C., 675
Kreidl, I., 468, 507, 862
Kreidl, Heller & Co., 508

Kreiss, B., 376
Kreitmair, H., 820, 821
Kremann, R., 425
Kremers, E., 515
Kresling, E. K., 887
Krestinskaya, V., 390
Krestownikoff, A. N., 686
Kretchmar, G. A., 46
Kretovich, V., 868
Kreusler, 610
Kreusler, H., 298
Kreveld, A. van, 271
Kringstad, H., 555
Krishnan, K. S., 224, 348, 352, 353
Krishnamurti, P., 149
Krizenecky, J., 851
Kröger, M., 593
Kröner, W., 124
Kroetz, C., 753, 754
Krogh, A., 740
Krollpfeiffer, F., 626
Kronenberger, A., 467
Kronenberger, P., 679
Kronfeld, P., 763
Kronig, R. De L., 228, 243, 374
Kroon, H. M., 837
Kropa, E. L., 538, 539
Krüger, O., 505
Krug, R., 449
Kruger, J. H., 780, 791
Krumpel, O., 674, 677
Krumpell, O., 188
Krupski, A., 690
Ku, Z. W., 307
Kublitskiĭ, A. M., 408
Kubowitz, F., 684, 687, 710
Kucera, C., 759
Kudssus, H., 817
Küch, R., 72, 84, 106, 107, 147
Küchler, L., 475
Kühne, H., 357
Kükenthal, H., 343
Kuen, F. M., 861, 862
Küster, W., 867
Küstner, H., 679, 688
Kufferath, A., 575
Kugelmass, I. N., 790
Kuhl, H., 410
Kuhn, H., 95, 237, 239, 240, 249, 275, 282
Kuhn, R., 413, 425, 685, 767, 810, 851, 852, 856
Kuhn, W., 45, 227, 266, 318, 320, 339, 349, 350, 461
Kuhrmann, F., 484
Kulteren, S., 839
Kultjugin, A., 755
Kumanomidoh, S., 682
Kumar, K., 874
Kummerer, L., 474, 645
Kunau, E., 371
Kunerth, B. L., 852
Kunerth, W., 201, 202
Kunz-Krause, H., 441, 443
Kunze, P., 136
Kunzer, W., 332
Kupinskaya, G. V., 346
Kurihara, K., 849
Kurotaki, S., 575
Kursanov, A. L., 874
Kurtz, H. F., 190
Kurz, P. F., 407
Kutzelnigg, A., 405, 589, 615, 678
Kuz'mina, K. A., 890
Kuz'mina, L. J., 588
Kwiencinski, L., 416, 432, 466

Labbé, H., 817, 831
Lacasagne, A., 707, 708
Lacell, H. G., 73, 76, 77, 80, 151
Lacey, B., 611
Lacey, B. S., 530
Lachat, L. L., 814
Lackey, R. W., 751
Ladenburg, E., 107, 193
Ladenburg, R., 293, 295
Ladewig, H., 448, 480-482, 882
Laffitte, P., 463
Lagerberg, O., 706
Lahousse, 801
Lai, C., 170
Laise, C. A., 142
Lakshminarayanan, A. K., 503
Lal, P., 362, 390
Lal, R. B., 267, 698
Laland, P., 849
Lamar, E. S., 82
Lamb, M. C., 650
Lambert, J. H., 206
Lambert, P. N., 188, 635, 642
Lambert, R. H., 381
Lambert, V., 673
Lami, R., 713
Lammert, O. M., 344
Lampert, U., 676
Lampitt, L. H., 559, 560, 831
Lamplough, F. E., 169, 170
Lambrechts, A., 479
Lambrey, M., 157, 271, 297, 324-326
Landau, L., 191
Landau, M., 394, 443
Landauer, R. S., 284
Landelium, E., 826
Landsberg, G., 224, 270, 317
Landsburg, K. G., 786, 790
Lane, C. E., Jr., 543
Lang, R. J., 33
Langbein, K., 47, 48
Langedijk, S. L., 404, 476
Langer, R., 812
Langhe, J. E. de, 271
Langley, S. P., 1
Langmuir, L., 31, 47, 48, 81-84, 89, 94, 209
Langstroth, G. O., 42
Langton, H. M., 832
Lantz, L. A., 635
Laquer, F., 808, 821, 851
Larché, K., 111
Lardy, G. C., 430
Larisch, L., 447
Larsen, C. J., 832, 840
Larsen, R. G., 489
Larsky, A. W., 256, 832, 840
Lasareff, P., 206
Lasareff, W., 458
Lasch, F., 820
Lasse, R., 176
Lassieur, A., 539
Lattey, W. T., 650
Lattre, J. de, 526
La Towsky, L. W., 51
Lau, E., 156
Lauchli, A., 297
Laucius, J. F., 792
Laudenklaus, H., 393
Laudet, G., 49
Laue, M. von, 7
Lauer, G. G., 602, 603
Lauer, K., 504
Laun, D. D., 50
Laurens, H., 202, 732, 733, 745-748, 754, 762, 769, 770, 774, 782, 818
Laurian, P., 467
Laurie, A. R., 776
Laurin, L., 612
Lauris, A., 305
Lavenets, I. V., 661
Lavin, G. I., 304, 305, 318, 683, 712
Lavoisier, I. J., 58
Lavrenenko, M., 593
Lavrov, F. A., 291
Lawrence, E. O., 157, 158
Lawrence, J., 193
Lazarev, P., 624
Lazlo, H. G. de, 153, 271, 501
Lea, C. H., 559, 560, 722
Lea, D. E., 722
Leadbetter, G., 76
Lease, E. J., 883
Leathwood, M. N., 176
Leavenworth, C. S., 884
Le Blanc, M., 80, 182, 209, 287, 331, 545
Le Bon, G., 127
Leboucher, P. J. M., 662
Le Bozec, L., 59
Le Bras, J., 508, 510
Leclerc, J. A., 560
Lecompte, J., 108
Lederer, B., 831
Lederer, E., 139, 853
Lederer, E. L., 390, 437, 554
Lederer, K., 139
Lederle, E., 338, 339
Lee, A. R., 788
Lee, Wei-Yung, 849
Leech, W. D., 853
Leendertse, J. J., 411
Leermakers, J. A., 405, 420, 428, 534
Lefebvre, H., 45
Leffmann, H., 364
Legris, R., 450
Lehfeldt, A., 483
Lehman, A. M., 772
Lehmann, E., 193, 295
Lehmann, G., 746
Lehmann, H., 178, 279, 339, 461
Lehmann, K. B., 727
Lehner, A., 707
Lehner, E., 741
Leiber, F., 632
Leifson, S. W., 281, 293, 298, 307, 308, 325
Leigh-Clare, J. L., 759, 790
Leighton, P. A., 44, 84, 96, 101, 103, 115, 121, 137, 320, 321, 349, 364, 378, 393, 401, 404, 415, 419-422, 464, 475, 480, 716
Leighton, W. G., 96, 137, 418
Leipunskiĭ, A., 231
Leiser, R., 530
Lemèche, M. R., 392
Lemoine, G., 272
Lemmers, E., 135
Lemon, H. B., 156, 170, 173, 196, 813
Lenard, P., 292, 386
Lenartowicz, J., 744
Lendle, A., 743
Lenher, S., 311-313
Lennox, E. A., 60
Lennox, F. G., 680
Lent, E. E., 283
Lenz, W., 225
Lenzi, F., 754
Leon, M., 601
Leonard, A. G., 40
Leonard, C. S., 853, 890
Leonicini, G., 891
Leopold, J. S., 825
Leo-Werke, 847
Lepeschkin, W. W., 750, 768
Lepskiĭ, S., 837
Lepsky, S., 838
Lerat, R., 817
Lerch, K., 682
Leroux, P., 373
Lesné, E., 761, 783, 784, 819
Lester, W. R., 176
Lesure, A., 522, 556, 726, 756
Leszynski, W., 380
Lettré, 809, 810, 813
Leulier, A., 792
Leupold, E., 602
Leuthardt, F., 671
Levaditi, C., 690, 712, 824
Levanas, L. D., 422
Lever Bros., 847
Leverenz, H. W., 265, 375
Levi, H., 264, 864

Levin, I., 852
Levine, A. A., 534
Levine, B. S., 758
Levine, V. E., 732, 818
Levinsohn, S. A., 783
Levinson, L., 776
Leviton, A., 447
Levshin, V. L., 370
Lévy, P., 566
Levy, S. A., 587
Lewis, B., 272, 274, 276, 280, 286
Lewis, G. N., 210, 294
Lewis, J. M., 775, 785, 814, 820, 838, 839
Lewis, M. D., 822
Lewis, M. R., 765
Lewis, R. C., 781, 824
Lewis, S. J., 155, 620
Lewis, T., 740
Lewis, W. C., 210
Lewis, W. C. M., 209, 347, 504
Lewkowitsch, E., 555
Lewschin, W. L., 262
Lex, E., 47
Ley, F., 271
Ley, H., 271, 351, 425, 428, 437, 441, 458, 476, 482, 495, 671, 674
Li, Y. P., 824
Liberalli, C. H., 481
Libby, W. F., 336
Lieben, F., 436, 449, 671-674, 676, 689, 702, 763
Liebesny, P., 745
Liebmann, G., 19
Lieck, H., 849
Lieneweg, F., 272
Liepe, J., 457
Lifschitz, S., 44
Lifschitz, I., 369, 464, 479, 500, 512, 626-628
Light, L., 479
Light, R. F., 709, 822, 833
Lignac, G., 740
Lillie, R. S., 717, 764, 865
Lilienfeld, W. E., 660
Lima, P. de, 885
Limaye, D. B., 478
Limaye, P. S., 361
Lind, S. C., 276, 278, 291, 414, 415
Lindberg, E., 432, 449
Lindemann, F. A., 209
Linden, H., 860
Linder, J., 829
Lindner, P., 709
Lindquist, F. E., 280
Lindström, C. F., 396, 425
Link, D. C., 81
Linnett, J. W., 423, 464
Linsert, O., 804, 807-809, 834
Lipmann, F., 451
Lipp, P., 515
Lippay, F., 865
Lippert, K. M., 860
Lippmann, A., 744, 745
Lishmund, R. E., 425
Lisse, M. W., 704
Lister, M. W., 461
Lister, W. N., 610
Little, C. C., 787
Liu, T.-K., 414
Liveing, G. D., 35, 294
Liversedge, S. G., 405
Livings, G., 611
Livingston, R., 259, 291, 341, 414, 415
Ljungkvist, G., 826
Ljungren, G., 493
Lloyd, B., 720, 721
Lloyd, W. V., 522
Lobb, D. E., 815
Locher, G. L., 101
Lochte-Holtgreven, W., 52, 244
Locke, F. J., 172
Locke, F. M., 168, 172
Lockyer, Sir N., 32, 35
Lodati, D., 472
Lodenkämper, H., 754
Loeb, L. B., 40
Loeb, M., 760
Loeb, S., 258
Löcker, T., 417
Loeffel, W. J., 786
Löhle, F., 378
Löhner, L., 750, 860
Loeper, M., 756
Loew, G., 557
Loewe, L., 436, 449
Loewen, D. F., 823
Löwenstein, L., 840
Loewi, O., 761
Loewy, A., 742, 750, 824
Lo Grasso, H., 770, 775
Lohaus, H., 484
Lohfert, H., 387
Lohmann, A., 803
Lohse, H. W., 35
Loiseau, G., 690
Lojkin, M., 830
Lombardi, L., 511
London, F., 163, 236
Long, B., 170, 176
Long, E. R., 823
Long, F. L., 874
Long, M., 128
Long, M. B., 97, 106, 107, 165
Long, N. L., 818
Long, S. H., 388
Loofbourow, J. R., 271, 698, 699, 701, 703, 708, 794, 804, 850, 851, 855
Loomis, F. W., 227, 243
Loose, L., 883
Lord Investierungs-Korporation, A. G., 660
Lorenz, A. J., 847
Lorenz, E., 768
Lorenz, H., 374
Lorenz, L., 355
Lorinser, P., 681
Lotte, P., 509, 608
Lotz, A., 366
Louis, P., 516
Loureiro, A. J. de, 556
Loury, M., 510
Louwsma, H. W., 883
Loveland, R. P., 379
Lovern, J. A., 555
Lovisatti, N., 740
Lowenstein, E., 690
Lowry, C. D., Jr., 653
Lowry, T. M., 68, 148, 244, 355, 395, 425, 451, 515, 522
Luber, A., 401
Lucas, F., 597, 714
Lucas, N. S., 736, 739, 779, 809, 847
Lucas, R., 450
Luce, E. M., 781, 835
Luce-Clausen, E. M., 773
Luckiesh, M., 34, 46, 141, 143, 144, 147, 165, 168, 195, 583, 642, 738
Luco Products Corporation, 172
Lucy, F. A., 475
Ludany, G., 689
Ludlam, E. B., 280, 282, 283, 287, 406
Lübcke, C., 94
Lübcke, E., 82
Lüers, H., 681
Lüppo-Cramer, 367, 376, 380, 381
Lütkemeyer, H., 276, 278, 279
Lüthy, A., 431
Lüttringhaus, A., 806-808, 821
Lumbard, V. G., 650
Lumière Brothers, 365
Lumière, A., 495
Lumière, L., 495
Lund, H., 849
Lunt, R. W., 310
Lundagen, M. A., 783
Lundé, G., 555
Lundegård, H., 35
Lupas, I., 475
Luszczak, A., 624, 651
Luten-Berg, K., 565
Luther, R., 182, 206, 214, 347, 348, 368, 504, 505, 524, 542
Lutz, R. E., 489
Luxat, K., 546
Luyet, B., 707, 708
Lyashenko, V. D., 500
Lyman, T., 7, 21, 22, 192, 381, 698
Lyons, E. H., 400
Lythgoe, R. J., 857, 859
Lyubimenko, V. N., 849, 874

Mabbott, E. E., 546
McAlevy, A., 517
McAlister, E. D., 96, 108-110, 718
Macaulay, R. M., 494
McBain, J. W., 588
McBeath, E. C., 824
McBee, E. T., 526
Macbeth, A. K., 343, 502
Macbeth, H. F., 657
McBride, G. C., 862, 863
McCaig, F., 330
McCaskey, D., 774
McCleland, N. P., 416, 431
McCloskey, K. E., 567
McCollum, E. V., 779, 835
MacConkey, C. A., 451
McConnell, J. R., 652
MacCormac, H., 772
MacCorquodale, D. W., 805, 856
McCrae, A., 890
McCrae, H. M., 772
McCurdy, W. H., 83
McDonald, F. G., 792, 794, 806, 807
MacDonald, G. D., 420
McDonald, J. K. L., 163
Macdonald, J. Y., 324, 325
McDonald, R. D., 406
Macdonald, R. F., 50
McDonough, E. G., 423
McElroy, K. P., 549
McEwen, H. D., 846
McEwen, J. L., 642
McFarlan, R. L., 853
McFarlane, W., 853
McGookin, A., 489, 495
McGowan, J. P., 818
McGregor, T., 273
McGroarty, W. J., 830
McGuigan, H. A., 523, 689
Macht, D. I., 268, 523, 658, 691, 735, 749, 865
Machti, A., 846
McHugh, G. P., 494
McIlwain, H., 522
McIntosh Electrical Corporation, 81
Macintosh, J., 836
Mack, E. L., 349
Mackay, C. A., 269
McKay, F. M., 818
Mackay, H. M. M., 789
McKeag, A. H., 142
McKee, R. H., 607
McKee, R. W., 856
M'Kenna, C. B., 350
McKenzie, H. M., 618
Mackenzie, K. H., 782
McKenzie, M. R., 774, 822
MacKenzie, T. C., 400
McKeown, A., 210, 228, 281, 296, 341, 351, 446
McKeown, S. S., 32
MacKeown, S. S., 48, 82
McKillop, M., 785
McKim, W. A., 589
McKinlay, D., 722, 831
McKinley, E. B., 712
MacKinney, G., 870
McLagan, H. P., 81
MacLean, I. S., 837
McLean, S., 143
McLennan, J. C., 317
MacLeod, F. L., 837-839
MacLeod, G. F., 718
McMahon, P. R., 623
McMahon, P. S., 285, 377
McMorris, J., 371
MacNair, W. A., 795, 813
McNamara, T. L., 655
McNaughton, F. E., 659
McNicholas, H. J., 155, 165, 179, 180, 856
McNulty, S. A., 466
Macovski, E., 472
McQuarrie, I., 790
MacQuiddy, E. L., 51
McRae, D. R., 42
Macwalter, R. J., 368, 856
McWillie, J., 296
Mada, T., 354
Maddison, R., 96, 107, 128
Maddison, R. E. W., 255, 346, 357
Maddock, A. J., 117, 188
Madelung, W., 626
Madhok, M. R., 351
Madinaveitia, J., 502
Maecker, H., 52
Magaldi, F., 529
Magee, H. E., 754, 784
Magill, M. A., 674
Magistris, H., 670
Magninini, G., 328
Magondeaux, B., 731
Mahajan, L. D., 555
Mahncke, H. E., 333, 413
Maier, Fr., 562
Maier, W., 624
Mailey, R. D., 829
Mainzhausen, L., 392
Maisin, J., 511
Majert, D., 369
Maki, T., 624
Makrineos, I., 754
Malachowski, R., 456
Malaviya, B. K., 497
Malaviya, K. N., 538
Malcolm, H. W., 46
Malczynski, S., 754, 755
Malley, R. D., 149
Malm, C. J., 621
Malowan, L. S., 743
Maltby, J. G., 64
Malus, E. L., 4
Mameli, E., 826
Manchot, W., 370
Manchot, W. J., 370
Mancini, J., 660
Mandelbaum, J., 857
Mandelstam, L., 224
Mandelstam, S. L., 53
Manecke, W., 564
Manen, B. van, 240
Mangini, A., 624
Mangold, E., 745
Mangold, P., 449, 516
Manicke, P., 441, 443
Manley, J. H., 160
Mann, M., 712
Mannich, C., 179, 182
Manning, W. M., 325, 428, 866, 876
Mansfield, J. V., 548
Manuel, S., 855
Maquenne, 715, 887
Marble, A., 819, 821
March, A., 9
Marchand, P., 651
Marchionni, A., 741, 752
Marchlewska, J., 388
Marchlewski, L., 416, 431, 432, 466, 478, 479, 482, 501, 670, 688
Marckwald, W., 268
Marconi, G., 6
Marcusson, J., 564
Marden, J. W., 140, 141, 149
Margaritov, V., 611
Marie, S. V., 630
Marini, M., 619
Marique, P., 862
Markar'yan, E. A., 790, 830
Marker, R. E., 792
Marks, H. P., 819, 821
Marling, P. E., 572
Marmeli, E., 710
Marmier, L., 358
Marras, F. M., 758
Marriott, G. J., 506
Marsh, J. K., 504, 511
Marshall, A. L., 257, 258, 281, 283, 284, 287, 301, 302, 797, 802, 803
Marshall, I. H., 816
Marshall, S. M., 767
Martin, A., 271, 856
Martin, E. K., 762
Martin, B. T., 715
Martin, H., 227
Martin, H. S., 167, 171
Martin, R. B., 655
Martin, R. C., 587
Martin, L. C., 165
Martin, W. H., 283
Martinelli, A., 823
Martinenghi, G., 555
Martini, E., 849, 852, 734, 761
Martini, V., 761
Martynoff, M., 478
Marx, A., 879
Marx, H., 774
Marzin, A., 481
Marzinovskii, E. J., 776
Masa G.m.b.H. zur Herstellung künstlicher Oberfläche, 648
Mascarelli, L., 511
Maschmann, E., 521
Mashimo, T., 693
Masland, W. E., 530
Maslowski, K., 64
Maslowski, M., 456
Mason, D. H., 745
Mason, F. A., 506
Mason, H. H., 745
Mason, R. B., 356
Mason, R. C., 47-49, 82, 93
Mass, E., 385
Massaroli, P., 826
Masseille, H., 576
Massengale, O. N., 787, 814-816
Massol, G., 400
Massol, L., 435
Masson, M. A., 152
Masure, M. P., 885, 889
Matheson, M. S., 426
Mathews, F. P., 861
Mathews, J. H., 103, 340, 345, 356, 364, 389, 443, 497
Mathieu, F., 819
Matignon, C., 194
Matiu, A. I., 631
Mathur, K., 253, 267, 486
Matthews, E., 283
Matthews, F. E., 407, 548
Matthews, F. L., Jr., 881
Matthews, M. A., 504
Matthias, F., 366
Matthies, W., 84
Mattill, H. A., 856
Mattler, J., 101
Matsunami, S., 405
Matsuoka, H., 837
Matsuoka, T., 849
Matsuyama, E., 95
Matushita, M., 757
Matusis, I. I., 743
Matzko, S. N., 837
Mauersberger, E. A., 556
Maughan, E., 788
Maughan, G. H., 775, 781, 787, 788
Maurarour, H., 36
Maurer, K., 679
May, B. W., 308
Mayer, E., 352, 706, 770-772
Mayer, F., 549
Mayer, G., 725
Mayer, H., 307
Mayer, J., 373, 432
Mayerson, H. S., 105, 202, 733, 745-748, 754, 759, 770, 782
Maynard, J. L., 399
Maynard, L. A., 754, 785
Mayneord, W. V., 556
Mayo, F. R., 545, 548, 550
Mayor, J., 722
Mayrhofer, K., 259
Maxwell, J. C., 6, 11, 16
Mazetti, C., 368
Mazurek, S., 610, 611
Mazza, F. P., 460
Mechlin, F. J., 124
Mecke, R., 193, 208, 225, 236, 237, 240, 246, 273, 297, 299, 326, 415, 417
Medard, L., 124
Medlar, E. M., 754
Meersseman, F., 823
Meerwein, H., 852
Mees, C. E. K., 178, 271, 381
Meesemaecker, R., 796
Meggers, W. F., 42, 190
Megrail, E., 690
Megraw, H. A., 505
Mehta, R. J., 873
Meidinger, W., 543, 544
Meier, F., 713, 714
Meiler, J. G., 348
Meissner, H., 346, 401
Meister, G., 141, 149
Mělka, J., 745
Mellanby, E., 795, 824
Mellanby, M., 780, 789, 824
Meller, B., 848
Meller, H. B., 98, 99, 201
Mellet, 663
Mellor, D. P., 280
Mellor, J. W., 282, 284-286
Melville, H. W., 135, 182, 265, 320-322, 325, 332, 394, 415, 584, 596
Melvin, E. H., 296
Mencke, E., 443
Mendel, L. B., 675
Mendelssohn, K., 378, 379
Mendum, W. C., 421
Mengoli, V., 824
Menke, J., 864
Menschick, W., 337, 338
Menzel, D. H., 191
Merck Chemische Fabrik, 832, 833
Merck, E., Co., 837
Merck, O., 635
Merkel, E., 183, 743
Merkel, H., 262
Merory, J., 660
Merriam, M. K., 546
Merritt, E., 624
Merry, J. J. F., 658
Mersereau, G., 533
Mertens, E., 458
Merz, A., 871
Merz, O., 564, 565, 590
Mesik, R. E., 757
Mesheristkaya, R., 750
Mestre, H., 871
Meunier, L., 622
Meyer, A. v., 511, 515
Meyer, F., 131
Meyer, I., 683
Meyer, J., 485, 486
Meyer, K., 451, 553, 812

Meyer, K. H., 596
Meyer-Betz, F., 861
Meyeringh, D. J., 597
Meyers, C. H., 258, 406, 563
Meyerstein, 750
Meyn, W., 129
Mezener, M., 370
Mezger, O., 663
Mezzadroli, G., 869
Michaud, G., 178
Michel, J. M., 657
Michel-Lévy, A., 36
Michels, M., 645
Michelson, A. A., 4, 5
Midgley, E., 615
Miethe, A., 97, 182, 366
Migita, M., 477
Mikami, H., 670
Mikeska, L. A., 655
Mikhailov, N. I., 612
Mikhailovski, S. M., 690
Miki, T., 572
Milanesi, E., 523, 848
Milas, N. A., 402, 405, 407, 517, 727, 832
Milbauer, J., 264, 498
Millam, L. H., 481
Millen, J., 173
Miller, C. C., 358
Miller, E. B., 652
Miller, E. S., 271, 854
Miller, G. A., 822
Miller, L. B., 151
Miller, R. C., 754, 785
Miller, R. D., 201, 202
Millikan, R. A., 7, 9, 42
Millprint Products Corp., 617, 727
Mills, A. G., 395
Milner, C. J., 150
Milner, S. R., 40
Milone, M., 461
Mindlin, S. S., 588
Mineral Separations N. Am. Corp., 655
Minganti, T., 444
Mingoia, Q., 517, 726
Minguin, J., 517
Minkowski, R., 559
Minor, J. E., 620
Minor, L. C., 585
Mironescu, E., 725
Mirsky, A. E., 676, 858
Mitamura, K., 836
Mitchell, A. C. G., 92, 150, 257, 258, 319, 321
Mitchell, C. A., 644, 663
Mitchell, H. F., 784
Mitchell, J. M., 836, 842
Mitchell, J. S., 265, 676, 677
Mitchell, J. W., 422, 889
Mitchell, S., 515
Mitra, B. N., 515, 670
Mitra, M. N., 484
Mitscherling, W. O., 657
Mitter, B. N., 440
Mittra, R. N., 370
Miura, K., 434
Miyamoto, S., 392
Miwa, T., 684
Miyanishi, M., 40, 273, 301, 304
Mizuno, K., 712
Mizusawa, H., 686
M. L. P., 600
Mobley, R. L., 710
Mochan, I., 318
Modern, F., 691
Möller, E. F., 809, 810
Moelwyn-Hughes, E. A., 298, 335
Mörikofer, W., 801
Moewus, F., 767
Moffet, G. L., 809
Mohammad, S. S., 869
Mohile, B. V., 361
Mohler, F. L., 109
Mohr, F., 205
Mohr, W., 839
Mojen, H. P., 594
Moldenhauer, O., 872
Molinari, 471
Molisch, H., 874
Moll, T., 814, 821
Moll, W. J., 96
Mollney, E., 611
Mollwo, E., 373
Molnar, E., 673
Molnar, J., 499
Molnar, N., 728
Molodenskii, V. S., 612
Momose, I., 586
Monasterio, G., 865
Moncetz, A. de., 209
Mond, R., 675, 676
Monden, S., 553
Monier, J. A., Jr., 510
Montagne, P., 45
Montagne, R., 382
Montfort, C., 873, 882
Montgomery, B. E., 824
Montgomery, C. W., 310, 315
Montgomery, M. E., 822
Monti, L., 474, 482
Montignie, E., 367, 370, 812
Montsanto Chemical Co., 481
Monvoisin, 724
Moody, C. A., 786
Mooney, R. B., 406, 457
Moor, F., 389
Moore, A. R., 767
Moore, B., 151, 695, 867-869, 881, 882
Moore, C. N., 798, 804
Moore, E. E., 688
Moore, H. R., 109
Moore, J. G., 887
Moore, J. M., 787
Moore, M. B., 688
Moore, McF., 132
Moore, T., 555, 791, 821, 822, 856
Moore, W. G., 50, 59
Morabito, F., 777
Morales-Otero, P., 706
Moran, W. H., 753
Morelle, J., 819
Morey, G. H., 447
Morgan, A. F., 786, 818, 819, 823, 848
Morgan, H., 188, 693
Morgan, J. L. R., 344, 357
Morgan, W. L., 561, 562
Morgareidge, K., 846
Morgen, R. A., 847
Morgulis, S., 685
Mori, H., 621
Morikaw, K., 394
Moritz, A. R., 754, 755, 790
Moritz, H., 64
Morrell, J. C., 652-654
Morrell, R. S., 456, 564
Morris, H. L., 601, 609, 610
Morris, J. C., Jr., 269
Morris, N., 819
Morris, V. N., 600
Morrison, C. G. T., 391
Morrison, R. R., 798, 803
Morse, D. S., 611
Morse, M., 792, 794, 801
Morse, P. M., 31, 236, 374
Mortenson, R. A., 464
Morton, D. S., 365, 524
Morton, R. A., 97, 102-104, 129, 351, 352, 368, 431, 495, 513, 555, 794, 795, 797, 804, 853-856
Moskalenskaya, E., 454
Moskovich, S. M., 384
Moss, J. E., 100, 103, 104, 127
Moss, W. H., 585
Mosset, M., 538, 541, 548, 549
Mossini, A., 826
Mott, N. F., 376, 379
Mott, W. R., 498, 527, 640
Mottram, J. C., 865
Mott-Smith, H., Jr., 31, 81
Motz, H., 376
Moufang, E., 725
Mougeot, P., 636
Mougey, H. C., 586
Mounier, D., 499, 633
Moureau, H., 451
Moureu, C., 423, 509, 511, 608
Mouriquand, G., 780, 781, 784, 792
Moycho, V., 737
Mrazek, S., 393, 394, 414
Much, 691
Mudrovcic, M., 353
Muffat, C., 478
Mühlhausen, C., 626
Mühlendahl, E. von, 587, 590
Muir, J., 663
Mukerji, B. K., 249, 252, 253, 259, 260, 337, 344, 351, 445, 446, 541
Mukerji, D. M., 360
Mukerji, S. K., 350
Mukherjee, J., 433, 541
Mukherjee, S. K., 883
Müller, A., 424, 520, 646
Müller, C., 464
Müller, E., 401, 413, 439, 510, 638
Müller, F. G., 415
Müller, H., 283, 411
Müller K. O., 550
Müller, K. L., 401, 407, 535, 538
Müller, M., 810
Müller, R. H., 260, 262, 354, 388, 443, 449
Müller, R. W. J., 752
Müller-Rodloff, I., 510
Müller-Skjold, F., 137
Mulliken, R. S., 225, 226, 228, 325, 396, 412
Mumford, L. S., 310
Mumm, O., 261
Munch, R. H., 160
Mund, W., 320
Mündell, O., 792
Münzinger, W. M., 591
Munsell, H. E., 787, 814
Muntwyler, E., 684
Munzert, H., 564, 572
Murakami, R., 683-685, 709
Murakawa, K., 92
Murarour, H., 354
Murat, M., 423
Murayama, M., 753, 758
Murgulescu, I. G., 368, 442
Murke, H., 805
Murphy, E. F., 787
Murphy, G. B., 653
Murphy, G. M., 158, 159
Murphy, R. V., 389
Murray, G. H., 167
Murray, J. M., 787, 836
Murray, T. F., 591, 592
Murthi, D. S. N., 485, 536
Murthi, M. L. N., 486, 538
Murty, K. S., 351, 354, 503
Musante, C., 852
Muskat, M., 163
Mussehl, F. E., 814
Myer, J. L., 46, 47
Myers, A. E., 323
Myers, V. C., 684
Mynster, E. H., 179
Myrbäck, K., 793

Nabarro, D., 855
Naef, R., 852
Nagai, I., 600
Nagai, Y., 347
Nagaoka, H., 50, 149, 366
Nagle, P. G., 600
Nakadate, K., 760
Nakae, R., 825

Nakamura, A., 368
Nakamura, G., 95, 275
Nakamura, H., 881
Nakamura, K., 274
Nakamura, M., 558, 559
Nakamura, Y., 678
Nakashima, M., 857
Nakashima, T., 587
Nakayama, A., 506
Nakayama, Y., 690
Nanavutty, S. H., 711
Nandy, S. K., 418, 421
Narasimhaswami, M. V., 268, 367
Narayana, T. S., 273, 283
Narayanan, B., 467
Narayanaswamy, L. K., 348, 353
Narayanmurti, D., 449, 481
Nastyukova, O. K., 717
Natelson, S., 545, 805, 811, 832
Nath, B. V., 351
National Carbon Co., 54-63, 173, 664, 829
National Research Council, 96, 227, 265
Naton, J., 493
Naudé, S. M., 329
Naumann, H. M., 68
Naumann, K., 622
Naunton, W. J. S., 599, 605
Nauroy, A., 581, 589
Navez, A. E., 268
Neave, A. S., 388
Neckel, 452, 482
Negelein, E., 687, 874, 876
Negishi, M., 587, 621
Negresco, T., 42
Neher, P., 357
Neiger, R., 451
Neilsen, C., 853
Nekludov, V. N., 625
Nekrasov, N. I., 874
Nelles, M., 466
Nelson, A. F., 536, 537
Nelson, E. M., 793
Nelson, H. A., 128, 556, 575, 577, 578, 580, 590
Nelson, M., 814
Nelson, M. T., 780
Nelson, R. E., 531
Neracher, O., 816
Nernst, W., 191, 206, 212-215, 283, 284, 287, 289, 292
Nestler, R. B., 787
Nettmann, P., 581
Neuber, F., 661
Neuberg, C., 361, 431, 432, 448, 449
Neudert, W., 518
Neuerburg'sche Verwaltungs Gesellschaft, 659
Neuhaus, C. J., 49
Neuhäusser, A., 42
Neumin, H., 231, 238, 240, 241, 244, 300, 402
Neumann, L., 537
Neumann, W., 690
Neuroth, H., 648
Neuschul, P., 451
Neuweiler, C., 339, 630
Neuwirth, R., 254, 864
Neville, G. H. J., 298
New, G. F., 576, 583
Newcomber, H. S., 693
Newell, J. M., 712, 887
Newman, F. H., 32, 83, 163
Newton, E. B., 679
Newton, I., 3
Ney, L. F., 867
Nicholes, P. M., 354
Nicollier, 344
Nicholls, A. G., 767
Nicholls, H., 832
Nichols, A. C., 860
Nichols, E. F., 6, 183
Nichols, E. L., 19, 265
Nichols, J. B., 181
Nickelsen, O., 740
Nicol, J., 48
Nicola, O., 809
Nicolaysen, R., 818
Nicolet, B. H., 447, 541
Nicolet, G., 343, 344, 485, 488
Nicolic, D., 353
Nicolson, D. G., 572
Nicolson, M. G., 140
Niederhauser, 636
Niederhoff, P., 431, 451
Niekerk, J. van, 800, 811, 815
Nielson, H., 830
Nies, N. P., 400, 536
Nigudkar, K. D., 361
Niimiya, H., 643
Nijveld, W. J., 853
Nikiforov, A. Y., 82
Nikiforov, V.-K., 392, 408
Nikitine, S., 383
Nikolai, F., 171
Ninomiya, R., 758
Nisbet, J., 81
Nishioeda, M., 877
Nishizawa, Y., 385, 589
Nitchie, C. C., 64, 175
Nitschke, A., 826
Nitta, B., 865
Nitzescu, I. I., 727, 793, 819, 822
Noack, K., 261, 498, 862
Noddack, W., 209, 211, 215, 377, 381, 532
Noel, L. von, 846
Nogemi, Y., 706
Nogier, T., 127, 720
Nolf, L. O., 718
Noll, A., 620
Nomura, R., 831
Nonaka, M., 564
Nonidez, J. F., 755
Nordenson, H., 387, 388
Norris, E. R., 855
Norris, R. J., 708, 726, 828, 855
Norrish, R. G. W., 247, 248, 258, 285-287, 289, 290, 298, 302-304, 326-329, 406, 416, 417, 419-422, 425-427, 429-431, 457, 460, 461, 524
Northrop, J. H., 683
Northrup, E., F., 48
Norton, A., 261
Norton, B. M., 397, 398
Norton, J. F., 704, 720
Notevert, O., 853
Nothaas, R., 745
Nottingham, W. B., 46-48
Novacek, E., 556
Novak, F. J., 776
Novikov, V. A., 890
Novotny, C. K., 597
Noyes, W. A., Jr., 214, 228, 236, 294, 295, 302, 318, 319, 324, 325, 333, 348, 413, 417, 425, 426, 428, 429, 439, 441, 447, 543
Noyons, A., 764, 858
Nozicka, F., 468, 507, 862
Nurnberger, C., 629
Nussbaumer, T., 560
Nussmeier, M., 806, 814
Nutting, P. G., 74
N. V., Chemische Fabrik L. van der Grinten, 105
N. V. Elektrochemische Industrie, 360
N. V. Philips Gloeilampenfabrieken, 77, 139, 141, 142, 149, 150, 156, 171, 172, 479, 646, 648, 829, 833, 834

Oakwood, T. S., 792
Oana, M., 761
Oatway, W. H., 823
Oberhauser, F., 445
Oberto, S., 601
Obreimov, I. V., 336, 501, 504, 624
O'Brien, B., 57, 193, 832, 846
O'Bryan, H. M., 617
Oda, R., 504
Oday, A. B., 144, 147
Oddo, G., 646, 647
Oertel, W., 348
Oettingen, W. F. v., 734, 751
Offant, C., 761
Ogawa, M., 751
Ogawa, W., 584
Ogg, R. A., Jr., 44, 320, 321, 349, 486, 546
Oguri, S., 111, 619
Ohl, F., 619
Ohle, H., 851
Ohlsen, H., 434
Ohlsson, E., 743
Ohmori, M., 625
Okamura, T., 685
Okii, I., 817
Okinaka, T., 530
Okubo, J., 95
Okuyama, K., 607
Olcott, H. S., 856
Olcovich, H. S., 856
Oldenberg, O., 163, 181, 182
Olivier, J., 756
Olivier, S. C. J., 546
Olson, A. R., 258, 318, 406, 412, 413, 445, 453, 454
Olson, T. M., 786, 835
Olsson, E., 244
Omar, W., 758
Omori, M., 500
Onoda, T., 311, 314
Onslow, G. A., 671
Ontario Research Foundation, 640
Oosterhuis, E., 146
Opisso, F., 807
Oppenheim, E., 831
Oppenheimer, F., 151
Orekhova, T. A., 885
Orelup, J. W., 743
Orlov, S., 776
Orlova, O. V., 587
Orndorff, W. R., 466, 504, 505
Orne, S. W., 51, 57
Ornstein, L. S., 48, 49, 52, 97, 210, 271
Ornstein, T., 755
Orr, A. P., 767
Orr, J. B., 754, 784, 786
Orr, W. J., 784, 785
Ort, J. M., 673
Orth, O. S., 402
Orton, K. J. P., 497
Os, D. van, 513
"Osa" participations industrielles, 169
Osborn, T. W. B., 103, 757
Oschchipkov, F. P., 168
Oser, B. L., 835
Oshima, G., 684
Oshima, Z., 677
Osipov, A. P., 890
Osram Co., 156
Ossenbrüggen, W., 293
Østby, O., 343
Oster, R. H., 707-709
Osterhout, W. J. V., 872
Ostrikov, M. S., 870
Ostrimuislenski, I., 409, 597
Ostwald, Wo., 876
Osugi, S., 350
Ott, H., 550
Ottensooser, F., 690
Ottmer, R., 372
Otto, B., 413
Otto, H., 851
Otto, M. P., 720

Ouellet, C., 439, 443
Owen, E. A., 115
Owen, J. R., 812
Owen, W. L., 710
Owens, J. S., 64, 662
Oxford, A. E., 549
Oxholt-Howe, H., 441, 444
Oya, T., 681

Pabst, E., 583
Pace, J., 684
Pace, N., 860
Pachioli, R., 824
Pacini, A. J., 617, 660, 828, 834
Packard, C., 732
Padelt, E., 297, 307
Padgett, F. W., 531
Padmanabhan, R., 426
Padoa, M., 250, 254, 255, 291, 441, 443, 444, 485
Padovani, C., 529
Page, I. H., 822
Page, L., 227
Pagel, H. A., 345
Paget, R., 147, 151
Paic, M., 690, 759
Paillard, H., 62, 533
Paine, C., 624
Paint and Varnish Research Lab., Berlin, 592
Pakschwer, A., 632
Pakshver, A., 615
Pal, N. L., 882
Palit, C. C., 432, 450, 553
Pallaske, G., 792
Pallu, R., 354
Palm, T. A., 778
Palmer, F., Jr., 208, 349
Palmer, L. S., 850
Palmiero, G. G., 709
Panchenkov, G., 602, 653
Pandalai, K. M., 458
Papcke, G., 742
Papp, S., 782
Pappenheimer, A. M., 779-781, 783, 856
Pardee, K., 772
Parisi, M., 75
Park, E. A., 779, 780
Parke Davis & Co., 659
Parker, A. E., 330
Parker, H. O., 653
Parkin, J., 868
Parkinson, N. F., 720
Parks, H. C., 566, 569, 578
Parsons, W. B., 1, 2
Parti, Y. P., 240, 395, 396
Pascal, P., 451
Paschen, 20, 22
Patat, F., 292, 300, 394, 402, 417, 420, 459, 475
Patek, A. J., Jr., 857
Patel, C. K., 616
Patent-Treuhand Gesellschaft für elektrische Glühlampen, 49, 137, 142, 150, 832
Paternò, E., 477, 533
Patitz, G. J., 709
Paton, R. F., 26
Patrick, W. A., 462
Patry, M., 463
Patten, C. G., 176, 358
Patterson, M. L., 60
Pattison, C. L., 824
Patton, I. J., 216
Patton, J. W., 777
Paul, B., 398
Pauli, W. E., 735, 737
Pauli, W., Jr., 25
Pauling, L., 378, 676
Pauthenier, 59
Pauthenier, M., 354, 463
Pavlik, M., 472
Pavolini, T., 363, 384, 450
Pawlikowski, J., 83
Payne, L. F., 787, 788
Payte, J. I., 751
Pazdor, F., 549
Peachy, S. J., 601
Peacock, P. R., 803, 854
Peacocke, T. A., 404
Peake, J. S., 64
Peakin, F. H., 494
Pearce, G. W., 890
Pearsall, W. H., 883
Pearson, A. M., 659
Pearson, T. G., 421, 429
Pech, J. L., 255
Peczalski, T., 57
Peden, O. D., 819
Pedrini, F., 476
Peek, A., 679
Peemöller, F., 691, 733, 744
Peierls, R., 372, 375
Peklo, J., 876
Pelletier, M., 451
Pelizzola, C., 605
Pelton, M. O., 190
Pennetti, G., 688
Penney, W. G., 374
Percival, W. C., 889
Perdrau, J. R., 860
Perel'man, T., 291
Perino, J., 722, 828
Perkin, A. G., 506
Perkin, F. M., 66, 74, 76, 720
Perkin, W. H., 488
Perkin, W. H., Jr., 547
Perkins, R. G., 720, 725
Perot, A., 5, 84, 273
Perret, A., 371
Perrin, F., 261
Perrin, J., 209, 262, 631
Perrot, R., 470
Perry, J. W., 190
Peskind, S., 773
Peskov, N. P., 179, 181, 182
Pestalozzi, S., 635, 644
Pestemer, M., 271, 337, 425, 467, 504
Peters, K., 537
Peters, R. A., 851
Petersen, W. F., 734, 751
Peterson, A., 624
Peterson, W. H., 831
Petter, C. K., 772
Petterson, A., 759
Pettersson, F., 760
Pettit, E., 198
Petri, W., 660
Petrie, G. F., 776
Petrikaln, A., 358
Pfaehler, K., 852
Pfannstiehl, W., 823
Pfannenstiel, W., 825
Pfeiffer, I., 530
Pfeiffer, J. P., 661
Pfeilsticker, K., 507, 876
Pferdemenges, H., 832
Pfister, M., 671
Pflüger, 106, 107
Pfrunder, N., 611
Pfund, A. H., 49, 372, 385, 386, 576, 582
"Pharmagans" Farm. Ins., 670
Phelps, D. V., 171
Phelps, W. M., 770, 772, 773
Philbert, A., 860, 861
Philip, G., 81
Philippe, M., 690
Philips Lamp Co., (see N. V. Philips Gloeilampenfabrieken)
Philipsky, A. J. H., 660
Philips Petroleum Co., 656
Philipson, J. B., 853, 854
Phillips, N. W. F., 127, 394
Phillips, R. A., 825
Philpot, J., 806, 821, 851
Phipps, T. E., 373
Physical Chemistry Research Co., 652
Piasecka-Zeyland, E., 823
Piatti, L., 127
Piaux, L., 412
Piccinini, C., 496
Pichler, F., 890
Pick, H., 682
Pickering, 32
Pickett, L. W., 209, 413
Pictet, A., 435
Pienkowski, S., 95
Pierce, E. W., 638, 643
Pierce, G. W., 77
Pierce, R. F., 66
Pierce, W. C., 443, 447
Pierucci, M., 59
Piggott, M. G., 174, 789, 834, 854
Pilar, F., 766
Pilkington Bros., Ltd., 170, 171
Pillemer, L., 684
Pincus, G., 124
Pincussen, L., 680-687, 703, 704, 745, 746, 751-756, 760, 830, 857
Pines, C. C., 364
Pink, H. R., 647
Pinoncelli, L., 559
Pinte, J., 635
Piper, J., 624
Pirani, M., 40, 47, 49, 115, 136
Pirie, N. W., 712
Pirrone, F., 432, 517, 710, 826
Pirschle, K., 868
Pisarzhevskiĭ, L. V., 253, 341
Pischulina, A. F., 625
Pittenger, P. S., 658
Pittsburgh Plate Glass Co., 167
Pitzer, E. C., 104, 444
Piutti, A., 366, 460, 516
Pizlo, J., 431
Planck, M., 10, 17, 21,
Platt, S. S., 742
Platz, H., 385
Plauson, H., 411, 584
Plaut, F., 849
Plaut, R., 744
Plisov, A. K., 496
Plokhotzkiĭ, E., 94
Plotnikow, J., 64, 205, 248, 255, 256, 292, 299, 305, 343, 360, 362, 364, 365, 377, 404, 409, 469, 522, 540, 634
Poddubny, W., 375
Podrouzek, R. N. V., 124
Poelt, H., 837
Poggi, R., 517
Pohle, H., 597
Pohl, R. W., 265, 372, 375, 378, 379, 795, 797-799, 808
Poincaré, J. H., 17
Poindexter, F. E., 378
Pokhil, A. I., 837
Polak, L., 243, 273
Polanyi, M., 265, 276
Polden, D. C., 649
Policard, A., 824
Polin, V., 31
Pollaczek, K. F., 675
Pollitzer, E., 416, 420
Pollock, B. E., 747
Pollok, J. H., 40
Poncher, H. G., 823
Ponomarev, F. G., 494
Ponte, M., 95
Ponthus, P., 679
Poole, H. H., 103, 108, 872
Popescu, C., 631
Popoff, M., 660
Popov, B., 238, 300, 309
Popoviciu, G., 793, 819, 822
Popovitzkiĭ, A., 365
Popp, H. W., 885-887, 889
Porcher, C., 670
Poremski, V., 188
Porret, D., 275, 370, 396, 404, 480, 487, 872
Porritt, B. D., 593, 599, 610
Porter, C. W., 425, 431, 437, 439, 478, 497, 869
Porter, J. M., 307
Porter, L. C., 144, 147
Porter-Levin, T., 830
Portheim, L., 873
Pospelov, A., 179, 390
Pospelova, K., 390
Post, C. I., 838
Postovskii, I. Y., 512
Potencier, R., 722
Potopenko, G., 42, 178, 182
Potter, 773
Potter, H. N., 293
Potterill, R. H., 360
Potthoff, P., 757
Potts, J. C., 287, 289
Pougnet, J., 367, 487
Poulter, T. C., 487
Povenz, F., 396, 425
Powers, G. F., 779, 780
Pozzi, L., 822
Pozzi, M., 672
Prachel, C. U., 588
Prager, M., 670
Prakash, O., 447
Prasad, M., 360, 361
Pratesi, P., 518
Prather, E. O., 814
Pratt, D. S., 479, 480
Pratt, E. L., 695
Pratt, M. C., 868
Pratt, R., 882
Praudière, E. de la, 428, 430, 477
Predwoditeleff, A., 317
Preiss, K., 620
Preiss, S., 646
Prescher, W., 860
Presnell, A. K., 826
Presslicht-Patent - Verwertungsgesellschaft, 60
Preto, E., 822
Preuss, L. M., 831
Preusze, K. H., 599
Pribram, R., 869
Price, W. A., 195, 786, 787, 831
Price, W. C., 396, 414, 416, 437, 467, 712
Price, T. S., 379
Prideaux, E., 624
Priest, G. W., 650
Priest, W. J., 546
Priestley, J. H., 868
Prigent, G., 318
Prik, E. M., 541
Prikhot'ko, A., 294, 501, 504
Prileshaeva, N., 464
Pringsheim, E., 285
Pringsheim, P., 261, 262, 264, 273, 443, 467, 665
Priou, R., 508
Pritchett, I. W., 825
Privault, M., 262
Probst, O., 490
Proft, H., 741
Proks, J., 695
Prosser, 66
Prouty, W. O., 141
Pruckner, F., 475, 849
Pucher, G. W., 884
Puchkovskii, B. S., 625
Püringer, K., 862
Pukall, W., 485, 486
Pulewka, P., 789
Pulkhi, L. H., 709
Pulman, A. O., 650
Pummerer, R., 593-595
Purcell, R. H., 358, 421, 429
Purkayastha, R. M., 253, 267, 362, 448, 450, 486, 540, 548
Purkis, C. H., 460, 461
Purvis, J. E., 416, 431, 476, 479, 482
Pusch, L., 211, 276
Putland, A. W., 557
Putschar, W., 821
Puxeddu, E., 361, 367
Puzenkin, E. S., 104, 452
Puzitschkii, K. W., 653
Pye, D. J., 618
Pyhälä, E., 651
Pyle, S. I., 789

Quaker Oats Co., 829
Quartz Fondu, 151
Quartz et Silice, 151
Quarzlampen-Gesellschaft, Hanau, 132, 725, 832
Quilico, A., 513
Quin, J. I., 860, 861
Quinlan, F., 385
Quinn, E. J., 853, 856
Quinquad, A., 754
Quint, F., 647
Qureshi, M., 340, 341, 428, 869
Qvist, W., 550

Raab, 860
Rabate, J., 432
Rabinovich, A. J., 381
Rabinowitsch, E., 228, 232, 233, 235, 242, 244, 273, 279, 335, 336, 345, 544, 872
Rabinovitz, L., 585
Raczynski, J., 778
Radley, J. A., 624, 645, 663
Radulescu, D., 460, 467
Radulescu, G., 654
Ragaz, Y., 533
Ragg, M., 586
Ragins, I. K., 813
Rahman, M. K., 340
Rahn, O., 696, 708
Rajewsky, B., 675
Rajvansi, A. R., 870
Rakestraw, N. W., 322
Rakshit, P. C., 432
Raleigh, J. T., 630
Ram, A., 194, 367, 860, 867, 869, 870
Raman, C. V., 224
Ramart-Lucas, Mme., 399, 412, 432, 453, 458, 467, 482, 494, 495
Ramp, D. G., 816
Ramsauer, C., 387
Ramsbottom, J. E., 69, 292, 293, 307
Ramsey, G. B., 711
Ramsperger, H. C., 431, 437, 439, 459, 478, 499, 869
Ramstetter, H., 173, 584
Ranc, A., 402, 403, 433, 434
Randall, J. T., 142
Randoin, L., 849
Rangcharya, T. L. K., 444
Ransford, R. B., 544
Rao, A. L. S., 364
Rao, B., 367
Rao, E. L., 268, 367
Rao, G. G., 193, 210, 247, 259, 350, 354, 458, 673, 869, 870
Rao, P. S., 503
Rao, R. H. R., 488
Rao, S. V., 358, 367
Rapieff, 66
Rapoport, M., 822
Rappaport, B. Z., 823, 824
Rasero, R., 770
Rasquin, H., 556
Rassweiler, G. M., 26, 663
Rast, K., 489
Rathemacher, C. P., 531
Rathenau, G., 298. 359, 382
Rathier, J., 662
Rathke, B., 463
Rathmann, F. H., 853
Ratsimamanga, R., 849
Rau, F., 489
Rauch, A., 624
Rauch, H., 796, 797
Ravault, P., 824
Ravensway, H. J., 564
Ravitz, S. F., 344, 363, 446
Rawling, S. O., 379
Rawlins, F., 239, 360
Ray, B. B., 450, 452
Ray, J. N., 522
Rayleigh, Lord, 16, 36, 48, 95, 193, 268, 592
Read, B. E., 849
Read, J. W., 723, 830
Rebière, G., 798, 804
Rebmann, A., 869
Recklinghausen, M. von, 73, 77, 78, 660, 720, 721
Recsey, E. v., 81, 829
Recsey, N. V., 81, 829
Redd, W. R., 727
Reddie, J. W., 853
Redman, R., 888
Reed, C. I., 703, 733, 735, 736, 746, 751, 753, 754, 785, 819, 822, 824, 826
Reed, M. C., 612
Reerink, E. H., 115, 142, 799, 801, 803, 805-808, 815, 829, 833
Reeve, L., 96, 107, 128, 246, 439, 441
Regener, E., 9, 292, 318
Regener, V. D., 193
Reggiani, M., 869
Regulski, H., 64
Rehman, R. A., 396
Rehren, I., 257, 302
Reich, V., 556, 665
Reichel, L., 511
Reichel, S. von, 810
Reichert, B., 743
Reichstein, T., 816
Reid, E. W., 579
Reid, H. G., 457
Reiff, O. M., 656
Reihlen, H., 124, 464
Reimann, A. L., 131
Reimer, M., 484, 491, 492
Rein, H., 635, 638
Reinartz, F., 515
Reindel, F., 796, 797
Reinders, W., 380
Reinemund, K., 852
Reiner-Deutsch, W., 728
Reinhard, M., 479, 803
Reincke, H., 414
Reiniers, J. H., 57
Reissaus, G. C., 359
Reiter, T., 57, 58, 821, 828, 829
Reith, F., 765
Reithmuller, C., 101
Rekling, E., 782
Reman, G. H., 877
Remennikova, V. S., 588
Remezov, I., 794
Remotti, E., 765
Rendell, L. P., 624
Renner, F., 507
Rennhard, A. W., 710
Renosto, G., 761
Rentschler, H. C., 97, 98, 141, 729
Renz, C., 350, 360
Repony, D., 610
Research Association of British Rubber and Tyre Manufacturers, 610
Retschinsky, T., 31, 72, 82, 84, 106, 107, 366
Retter K., 447

Rey, G., 622
Reychler, A., 344, 629
Reyher, P., 793, 820, 848
Reyn, A., 769, 770
Reynaud, 663
Reynolds, E. S., 688, 710, 889
Reynolds, F., 139
Rezzesi, F. D., 862
Rhinhold, J. S., 755
Rhodes, G. H., 616
Ribaud, G., 249
Ricard, R., 382
Rice, F. O., 210, 214, 303, 327, 339
Rice, G. P., 491
Rice, J., 210
Rice, O. K., 243
Richardson, A., 282, 376
Richardson, E., 592
Richardson, L. R., 850
Richardson, O. W., 156
Richardson, R. S., 192
Richter, C. M., 659, 828
Richter, G. A., 619
Richter, H., 77, 139, 829, 840
Richter, O., 873
Richter, V., 839
Rideal, E. K., 210, 258, 265, 274, 276, 280, 287, 319, 321, 329, 344, 542, 676
Rider, T., 828
Riding, R. W., 271, 351, 352
Ridyard, H. N., 108, 190
Rieche, A., 339
Ried, O., 556, 563, 662, 728, 828, 831, 840
Riederer, H. S., 526
Rienzo, A. de, 819
Riesenfeld, E., 366
Riesenfeld, E. H., 408, 644
Rigby, R., 60, 661
Riggert, K., 505
Right, R. E. De, 399, 537
Riising, B. M., 831
Rimington, C., 623, 861
Rimpel, H., 599
Ringer, W. E., 473
Rinse, J., 575
Rinskaja, E. S., 341
Ris, H., 635
Risak, E., 740
Risler, J., 183, 583, 743, 860, 861
Risse, O., 209
Ritchie, K. S., 360
Ritchie, M., 279, 283, 289, 290, 297, 300
Ritschl, R., 26
Ritson, K., 715, 885
Ritter, 6, 376
Ritter, E., 580
Ritter, J. J., 491
Ritter, W., 560, 562
Ritzenthaler, B., 429
Rivat, G., 539
Rivers, T. M., 712, 775
Rivière, C., 463
Rivkin, H., 785, 814
Roach, F., 64
Roadhouse, C. L., 835
Robert, E., 438, 455
Roberts, R. E., 814
Robertson, D. F., 825
Robertson, E. B., 849
Robertson, E. C., 775, 825
Robertson, H., 642
Robertson, J. D., 785
Robertson, R. M., 48
Robin, 724
Robinet, P., 516
Robinson, F. W., 60, 103, 832, 840
Robinson, H. A., 42
Robinson, R., 506
Robison, R., 818
Robl, R., 105
Robson, G. M., 822
Robuschi, L., 860
Rocard, Y. A., 59
Roche e Silva, M., 863
Roche, H. J., 785
Roche, J., 670
Roches, C., 384
Rochette, J., 742
Rock, E. N., 860
Rodebush, W. H., 217, 283, 530
Rodionov, S., 101
Rodloff, G., 352
Rodriguez-Ely, 720
Rodwell, R. V., 165
Roe, E., 809
Roehm and Haas Co., 584
Röhm, O., 584
Römer, R., 337
Röntgen, W. K. von, 7
Rössler, F., 97, 111
Rössler, G., 337
Roets, G. C. S., 861
Roffo, A. E., Jr., 742
Roffo, A. H., 669, 742, 766, 803, 815, 872
Rogai, F., 891
Rogers, A. O., 531
Roginskii, S., 318
Rogoski, W., 40
Rogovin, Z. A., 588
Rohde, H. W., 722
Rohr, F., 840
Rohr, H., 680
Rohrback, E., 565
Rojahn, C. A., 658
Rokhlin, G., 119
Rollefson, G. K., 214, 237, 244, 272, 280, 287-290, 298, 310, 312, 313, 315, 336, 418, 425, 440, 448, 532, 537, 539
Rollett, A., 410
Rollier, A., 770, 772-774
Rollwagen, W., 49
Rolph, F. W., 147
Roman, L. H., 418, 870
Roman, W., 687, 760
Romanova, K., 523, 776, 865
Romeyn, H., Jr., 333
Rompe, R., 47, 49, 83, 94
Roncallo, E., 733, 734
Rondoni, P., 790
Roof, J. G., 420, 424
Rooksby, H. P., 131
Root, R. W., 752
Rosanova, V., 853
Rosario, C. del, 713
Roscoe, 205, 206, 271
Roscoe, H., 285
Roscoe, M. H., 789, 836
Rose, C. H., 572
Rose, G., 171
Rose, M. von, 754
Rosebury, T., 824
Rosen, B., 273, 576
Rosenbach, J., 549
Rosenberg, W., 624
Rosenblatt, M. B., 824
Rosenblum, C., 414, 427
Rosenbohm, E., 479
Rosenfeld, P., 862
Rosenheim, A. H., 818
Rosenheim, O., 788, 789, 791, 792, 794-798, 804, 809, 810, 822, 853
Rosenmund, K. W., 546
Rosenstein, L., 656
Rosenthal, L., 589, 612
Rosenthal, J., 853
Roseveare, W. E., 445
Roskin, G., 523, 776, 865
Rosney, W. C., 431
Ross, J. C., 829
Ross, J. R., 775, 825
Ross, W., 38, 343, 361, 430
Rosseland, S., 193, 257
Rossem, A. van, 603
Rossi, A., 819
Rossi, G., 362, 629
Rossini, F. D., 241
Rossmann, E., 565, 566
Rossner, E., 674
Rost, G. A., 734, 769
Roth, E., 861
Róth, L. E., 868
Rothmann, A., 746
Rothmann, H., 734, 751
Rothmann, S., 752
Rothschild, P. de, 59
Rousseau, E., 104, 370, 434, 456, 555, 804
Rousseau, E. F., 727
Routh, I. B., 832
Roux, E., 692
Rowe, R. D., 422
Rowell, S. W., 405
Rowinski, P., 746, 754
Rowland, H. A., 4
Rowley, C. D., 256, 832, 840
Roxburgh, L., 332
Roy, N. C., 485
Roy, N. K., 449, 481
Roy, S., 390
Roy, S. C., 210
Royds, T., 40
Ruark, A. E., 228
Ruben, S., 139
Rubens, H., 6
Rubenstein, B. B., 268
Rubino, P., 822
Rudberg, E. G., 451
Ruddy, M., 708
Ruderman, A., 620
Rudolph, L., 853
Rudy, H., 851, 852
Rücker, C., 485, 491
Rüdy, R., 82, 236
Ruehle, A. E., 64, 851
Rühmekorb, F., 851
Ruess, H., 682
Rüttenauer, A., 142, 168, 175
Ruggli, P., 471
Ruhemann, M., 294
Ruinskaya, E. S., 253
Rump, W., 342, 355
Rundle, G. W., 577
Runge, C., 293
Runkel, K., 530
Runtzo, P. M., 408
Rupe, H., 476
Rupel, I. W., 786, 853
Rupert, F. F., 644
Ruppert, W., 718
Ruppol, E., 458, 798
Ruschig, H., 689
Ruska, J., 124
Rusleitner, K., 662
Russ, S., 693, 694, 697, 706
Russanow, A., 64
Russell, A. S., 405
Russell, E. E., 560
Russell, E. H., 715, 772
Russell, E. J., 286
Russell, G. R., 783
Russell, H. N., 24, 192
Russell, W. C., 175, 787, 814, 838, 856
Russell, W. K., 715, 769, 772
Rutherford, Lord, 21
R. U. V. Engineering Corporation, 829
Ruzicka, L., 809
Ryabinin, G., 288
Ryd, S., 449, 450
Rydberg, 20, 22, 23
Rydbom, M., 792, 822
Ryde, J. W., 52, 74, 142
Ryerson, L. H., 258

Rygh, A., 849
Rygh, O., 804, 809, 812, 815, 817, 849

Sabalichschka, T., 867
Sabatelli, V., 499
Sacchi, U., 754
Sacharoff, G., 860
Sachs, D., 369
Sachs, F., 472
Sachsse, H., 301, 310
Saeki, K., 860
Saha, M. N., 48, 193, 337
Saha, N. K., 396
Sahay, V., 546
Saidman, J., 733, 762, 776
St. John, C. E., 50, 192
St. Julian, R. R., 848
Saint-Maxen, A., 479
Saito, S., 608, 621
Saito, Z., 857
Sakai, S., 530
Sakuma, I., 586
Sakurai, S., 183
Saladini, G., 514
Salley, D. J., 303, 403
Salmon, W. D., 850
Salmon-Legagneur, F., 399
Salmony-Karsten, A., 169, 171, 829, 832, 840
Salo, A., 550
Salomon, H., 852
Salomon, K., 859
Salow, H., 295
Saltmarsh, M., 387
Saltmarsh, O. D., 425-427, 429-431
Salzberg, P., 592
Samant, K. M., 810, 873
Samec, M., 435
Samokhvalova, G., 837
Sampson, C. M., 774
Samuel, R., 240, 331, 337, 355, 395-397
Sanctis, A. G. de, 834, 841
Sandholzer, L. A., 712
Sandonnini, C., 443, 469
Sanford, H. N., 748, 825
Sannié, C., 188
Sanyal, R. P., 869
Sanzo, L., 432, 710
Sapozhnikov, D. I., 881, 882
Sarkar, P. B., 550
Sarkaria, A. R., 350
Sasaki, N., 274, 344
Sass, R. B., 395
Sassmann, H., 447
Sato, M., 573
Sattler, L., 447, 541
Savard, J., 479, 495
Savost'yanova, M. A., 378
Sawyer, R. A., 36, 42
Sayre, J. D., 888
Scagliarini, G., 514
Scal, C., 74, 359, 394, 514
Schaarchmidt, A., 506
Schachtschabel, K., 164
Schacken, J. M. G. de, 657
Schade, H., 740
Schadow, H., 744, 745
Schaefer, K., 270
Schaefer, V. J., 265
Schäfer, W., 549
Schaffner, M., 492
Schall, C., 498
Schall, L., 741
Schamberg, J. F., 756
Schamp, H. M., 763
Schanz, F., 448, 449, 675, 762, 763, 865
Scharlau, B., 823
Scharwin, W., 633
Schaum, K., 271, 388
Schaumann, H., 336
Scheele, K. W., 6
Scheer, 827
Scheibe, G., 42, 264, 337, 338, 351, 395, 396, 401, 425, 458, 593, 594, 624
Scheiber, J., 589
Scheibler, H., 541
Scheidt, E. O., 722
Scheiferle, B., 274
Schenck, C. C., 41
Schenck, F., 813, 816, 834
Schenk, P. W., 288-290, 305, 330, 385
Schering-Kahlbaum A.-G., 77, 431, 689
Scherz, F., 871
Scheunert, A., 790
Scheurer, A., 614, 638
Schieblich, M., 790, 792, 838
Schiflett, C. H., 414, 415
Schimkus, B., 804
Schindler, A., 840
Schipp, L. T., 401
Schippers, J. C., 819
Schirmer, H., 584
Schischliaiewa, S., 776
Schlägel, H., 359
Schlaer, S., 859
Schlager, M., 388
Schlayer, C., 710
Schlechter, E., 738
Schleede, A., 366, 384
Schleip, W., 718
Schlemmer, F., 562
Schlenk, F., 687
Schlenk, W., 626
Schlessinger, L., 398
Schlessinger, M., 271
Schlitter, E., 852
Jos. Schlitz Beverage Co., 722
Schlivitch, S., 503
Schlotthauer, C. P., 861
Schlubach, H., 432
Schlutz, F. W., 792, 794, 801, 830
Schmallfuss, H., 553, 559, 740
Schmick, H., 49
Schmid, H., 248
Schmid, R., 308
Schmiderer, L., 476
Schmidlin, J., 626
Schmidt, G., 271, 882
Schmidt, H., 447
Schmidt, H. J., 541
Schmidt, H. O., 826
Schmidt, J., 624, 689
Schmidt, K., 174
Schmidt, M., 856
Schmidt, M. E. A., 657
Schmidt, M. P., 648
Schmidt, O., 809
Schmidt, R., 378, 454, 455
Schmidt, R. W., 48
Schmidt, W., 92
Schmidt-Nielsen, S., 684
Schmidy, A., 124
Schmitt, P., 396
Schmitz and Co., 547
Schmitzler, E., 532
Schmorl, G., 778
Schmutz, F. C., 175, 556, 578, 580
Schmutz, R., 346, 539
Schnegg, H., 720
Schneider, E., 263
Schneider, E. G., 7
Schneider, H., 183, 246, 726, 828
Schneider, M., 361, 826
Schneidewind, A., 744
Schnider, A., 480
Schoder, F., 867
Schömmer, F., 365, 384
Schoeld, E. A., 341
Schön, M., 83, 592
Schoen, M. J., 575
Schönbein, C., 292
Schönberg, A., 464, 505, 509, 510
Schoenholz, L., 820
Schoenleber, F. C., 846
Schönrock, O., 68
Schöpp, K., 849, 852
Schoetzow, R. E., 652
Schoffstall, C. W., 188
Schofield, H., 569
Schofield, R. K., 228
Scholefield, F., 616
Scholl, H., 377, 828
Scholl, R., 507, 518, 522
Scholtz, F., 483
Schoorl, N., 396
Schoppee, C. W., 493
Schopper, T., 609
Schorigin, P., 469
Schormüller, J., 445
Schott and Co., 168
Schottky, W., 84, 93
Schou, S. A., 416, 419, 431, 432, 525, 651
Schour, I., 824
Schpolski, E., 335
Schrader, F., 376
Schreiber, E., 821
Schroeder, H., 658
Schrödinger, E., 10, 26, 226
Schroeter, G., 432, 511
Schroeter, M. P., 888
Schröter, W., 624
Schuberth, K., 690
Schübel, K., 837
Schüler, H., 26, 151, 163
Schütze, H., 410
Schuknecht, W., 792
Schuler, R., 847
Schulman, J. H., 265
Schultz, C. T., 281
Schultz, F., 851
Schultz, G., 471, 472
Schultz, O., 840, 841
Schultze, G., 589
Schultze, G. R., 312, 536
Schultzer, P., 783, 784
Schulz, H., 587, 590
Schulz, M., 579
Schulz, P., 94
Schulze, B., 26
Schulze, F., 386
Schulze, G., 612
Schulze, W. A., 656
Schulzer, P., 779
Schumacher, H. J., 296-298, 306, 307, 310-314, 316, 346, 349, 394, 395, 401, 407, 510, 526, 532, 533, 535-538
Schumacher, L., 685
Schumann, V., 7, 293
Schumm, O., 624
Schupp, E., 635
Schuster, A., 40
Schwab, G. M., 532
Schwarschild, K., 220
Schwarz, F. K. T., 860
Schwarz, H., 743
Schwarz, M., 404
Schwarz, R., 332, 333, 363, 368, 376
Schwarzenbach, G., 849
Schweckendiek, C., 479
Schweinitz, H. D. von, 357
Schweitzer, E., 42, 662
Schweitzer, H., 284
Schwenk, E., 431, 514
Schwerin, K., 674, 675
Schwob, M., 450
Scimone, V., 758
Scott, G. H., 822
Scott, H. T., 836

Scott, J. R., 608
Scott, K. G., 865
Scott, W. D., 474
Sears, H. J., 727
Sears, W., 131
Seberger, M. V., 818
Secareanu, S., 475
Secchi, C., 733
Seceroy, S., 744
Seed, L., 823
Seel, H., 766
Seel, P. C., 591
Seeliger, R., 48, 49, 82, 83
Seeling, K., 838
Seibert, F. B., 690
Seide, J., 718
Seide, O., 503
Seitz, E. O., 857
Seitz, F., 265, 375, 385
Selden Co., 481, 545
Seldeslacht, A., 757
Seligsohn, F., 685
Sellards, S. W., 862
Semashko, V., 837
Semb, J., 617
Semenoff, N., 214, 303, 340
Semmens, E. S., 267, 268, 882
Semp, H., 522
Sen, H. K., 682, 684
Sendlinger Optischer Glaswerke, 167, 171
Senftleben, H., 231, 257, 302
Senftner, G., 660
Sen-Gupta, D. N., 550
Sen-Gupta, P. K., 324, 395
Sen-Gupta, S. B., 624, 625
Serfass, E. J., 651
Servigne, M., 142, 152
Seshacharyulu, E. V., 350
Seshadri, T. R., 488, 503
Setz, P., 808
Seuss, A., 552
Sexton, W. A., 804
Seybold, A., 870, 888
Seyderhelm, R., 748
Seyewetz, A., 365, 495, 499, 633
Seymour, M. W., 485
Shanassy, H., 869
Shapiro, C. V., 164, 466
Shaposchnikoff, A., 31, 82
Sharf-ud-Din, 396
Sharma, B. S., 358
Sharma, R. S. 304, 339
Sharp, D. G., 695
Sharp, J. F., 328, 329
Sharp, P. F., 848
Sharp, W. E., 531
Sharpless, G. R., 704
Sharvin, V. V., 615
Shattock, F., 741
Shaver, W. W., 294
Shaw, H. F., 789
Shear, M. J., 785, 792, 822, 823
Sheard, C., 167, 512, 727, 763, 766, 788, 861, 885
Sheboldaeva, A. D., 860
Sheets, O., 780
Shekhter, A., 318
Shelling, D. H., 792, 820, 824
Shelow, E., 804
Shelton, H., 366
Shenstone, A. G., 24
Shenstone, W. A., 282
Shepard, N. A., 601, 609, 610
Shepherd, R. S., 581
Sheppard, S. E., 369, 376, 377, 379-382, 679
Sheremet'ev, G., 261
Sherill, M. S., 295
Sherman, A., 812
Sherman, E., 785, 792, 793, 836
Sherman, H. C., 780
Sherrill, M. L., 413
Sherts, J. H., 411
Shibata, K., 877, 882
Shibata, Y., 337, 479, 670
Shidei, J., 358
Shidei, T., 585
Shile, V. N., 652
Shilov, E. A., 346
Shimada, J., 849
Shinohara, U., 40
Shinozaki, Y., 573
Shin-Piaw, C., 297
Shipley, P. G., 779
Shirley, H. L., 888
Shishacow, W., 209
Shishlovskiĭ, A. A., 504
Shlaer, S., 271
Shljivic, S., 353
Shmidt, Y., 411
Shneer, I. M., 591
Shoda, M., 106
Shohl, A. T., 785, 846
Shoji, Y., 762
Shomura, J., 586
Shono, T., 584
Shoruigan, P. P., 521
Shpolskiĭ, E. V., 261, 444, 445
Shrader, J. H., 835
Shrewsbury, C. L., 855
Shrum, G. H., 853
Shrum, G. M., 176
Shtern, E. A., 887
Shugladze, A. K., 860
Shull, C. A., 867
Shumway, E. D., 829
Shutt, W. J., 295, 296
Shvartz, A. S., 341
Sibilia, C., 711, 885
Sibiryakova, G. N., 411
Sickman, D. V., 459
Sidoli, E., 746
Sidwell, A. E., Jr., 271, 858
Siedentopf, K., 282
Siegel, J., 785
Siegler-Soru, E., 352
Siemens, W., 66
Siemens and Halske, A.-G., 58, 135, 150
Siemens-Schuckert Werke, 60
Siemens-Werke, A.-G., 366
Sieper, G., 308
Sieplein, O. J., 581
Sigal, F. S., 385
Sigg, W., 476
Sigmund, F., 424, 473
Silber, P., 393, 449, 468, 470, 474, 476, 491, 493, 496, 511, 515, 517
Silbermann, J. T., 284
Silberrad, O., 545
Silberstein, L., 379
Silica Syndicate, Ltd., 151
Silverman, A., 170
Simard, R., 627
Simmonds, N., 779, 780
Simmons, N. L., 333, 354
Simola, E. J., 613
Simon, H. T., 46
Simon, R., 780
Simon, W., 485
Simona, E. J., 816
Simonds, E., 816
Simonis, W., 873
Simonnet, H., 669, 750, 790, 795, 798, 819, 823, 860
Simons, L., 209
Simpkins, G. W., 853
Sinclair, R. D., 747, 786
Singer, E., 856
Singh, B. K., 268, 515, 516
Singh, B. N., 874, 887
Singleton, F., 882
Singleton, W., 51
Sinha, P. C., 391
Sirch, C. W., 720
Sirian Lamp Co., 139
Sisley, P., 645
Six, G., 386
Skarzynski, B., 688
Skau, E. L., 817
Skaupy, F., 19
Skaupy, L., 85
Skinner, S., 367
Skorko, E., 273
Skrabal, A., 276
Skvortzov, S. S., 874
Slator, A., 542
Slepian, J., 32, 48, 49, 82
Slipher, V. M., 194
Slotin, L., 304
Slotta, K. H., 689
Smakula, A., 373, 380, 406, 453, 488, 490, 565, 798, 799
Small, J., 819
Smedley-Maclean, I., 789, 795
Smekal, A., 374
Smelt, J. A., 171
Smetana, H., 860, 863
Smiles, S., 493
Smiley, D. E., 775
Smith, A. E., 161-163
Smith, A. L., 623
Smith, A. R., 825
Smith, A. T., 718
Smith, A. W., 167
Smith, C. A., 835, 838
Smith, D. F., 210, 527, 530, 531
Smith, D. M., 535, 662
Smith, E. C., 711
Smith, E. L., 855, 873, 881
Smith, E. M., Jr., 770
Smith, E. W., 643
Smith, F. C., 670
Smith, F. C., 271
Smith, F. D., 481
Smith, F. F. P., 457
Smith, F. R., 42
Smith, H. A., 299, 300, 305, 663
Smith, H. D., 176, 358
Smith, H. H., 779, 788, 789, 792, 795, 847
Smith, H. P., 543
Smith, J. B., 814
Smith, J. H., 777
Smith, J. H. C., 418, 419, 854
Smith, L. A., 690
Smith, L. E., 588
Smith, L. L. W., 848
Smith, L. W., 174, 789
Smith, M. A., 653
Smith, M. C., 856
Smith, N. D., 161
Smith, W., 269
Smith, W. C., 636, 637
Smits, A., 206, 299
Smull, J. G., 554, 567, 568
Snelling, W. O., 530
Snitter, P., 587
Snoke, H. R., 661
Snow, C. P., 360, 416, 424, 808, 848, 849, 854
Snow, O. W., 882
Snow, R. D., 407
Snyder, C. D., 732
Snyder, R. M., 722
Snyder, V. D., 155
Soames, K. M., 780, 789
Sobel, A. E., 805, 832
Sobel, J., 819
Sobue, H., 617

Soc. anon. de Saint-Gaubain, Chauny et Cirey, 176
Soc. anon. les usines Rémy, 829
Soc. anon. pour les Applications des Gaz Rares etablissements Claude-Paz et Silva, 36, 142
Soc. d' Exploitation des Procédés d'Impression Sardou, 599
Soc. des usines chimiques Rhône-Poulenc, 562, 592, 833
Soc. Le Serment, 721
Soc. pour l'ind. chim. Bâle, 62
Söderbäck, E., 457
Söderman, M., 381
Söhngen, N. L., 710
Söll, J., 530
Soer, J. J., 846
Soeur, R., 822
Sohoni, N. V., 361
Solechnik, N. Y., 562
Sollazzo, G., 469, 471
Solmssen, U., 854
Solodovnik, 657
Solomon, A. K., 466
Solomon, S., 873
Soltan, A., 68
Solvay Process Co., 545
Somerville, P. G., 656
Sommer, H., 562, 613, 614, 623, 645
Sommer, J. J., 46
Sommerfeld, A., 23, 228
Sommermeyer, K., 238
Sonkins, S., 72
Sonne, C., 717, 734, 744, 750, 779, 782, 783
Soos, M., 759
Sostmann, H., 341
Sotto, G. E. de, 357
Souder, W. H., 107
Souty, P., 435
Sovalova, A., 582
Spanner, H. J., 131, 133, 149
Sparre, F., 530
Speakman, J. P., 623
Spealman, C. R., 629, 760, 862, 864, 865
Spear, E. B., 388
Speas, W., 624
Speer, J. H., 805, 822
Spence, C., 773
Spence, D., 596
Spence, J. C., 820
Spence, K. C., 800
Spence, R., 397, 427
Spencer, D. A., 647
Spencer, L., 347
Sperti, G., 147, 183, 246, 708, 726, 828
Spickard, V. W., 838
Spiegel-Adolf, M., 669, 674, 675, 677, 690, 733, 739
Spies, T. D., 823
Spietschka, W., 648
Spiller, J., 601
Spindler, H., 72
Spinka, J., 854
Spinks, J. W. T., 297, 298, 307, 348
Spitta, T., 308
Spoehr, H. A., 866, 869, 871, 874
Spohn, H., 877
Spolverini, L. M., 722
Sponer, H., 228, 235-237, 242, 244, 273, 275, 282, 293, 317, 325, 330, 331, 372
Spong, A. H., 355
Spooner, L. W., 190
Spranger, 821
Sprenger, G., 296
Spring, F. S., 805, 809, 810, 853
Springer, J. F., 720
Spychalski, R., 388
Squire, G. V. V., 287, 288
Squires, B. T., 860
Srinivasan, M. K., 550
Staats, E. M., 182
Stacey, R. S., 819
Stafford, G., 165
Stähler, F., 674
Stair, R., 99, 109, 147, 165, 166, 174, 175, 188, 195, 738
Stamberger, P., 558
Stambovsky, L., 743
Stamm, A. J., 617
Stammers, A. D., 103
Stammreich, H., 78, 149, 366
Stamsö, K. K., 828
Stancati, A., 754
Stanco, Inc., 562
Standard Brands, 563, 833
Standen, G. W., 64, 574
Stănescu, P. P., 874
Stange, O., 816
Stanley, W. M., 712
Stansfield, R., 413, 656
Stark, J., 31, 81, 82, 147, 207, 214
Starkie, D., 167, 169, 173
Stasiw, O., 374
Stateler, E. S., 720
Staud, A. H., 64
Staud, C. J., 591, 592
Staude, H., 593
Staudinger, H., 429, 602, 603
Stauffer, J. F., 876
Steacie, E. W. R., 127, 394
Steadman, F., 509
Stearns, G., 819
Steck, I. E., 785, 822
Stedman, H. L., 675
Steel, C., 431, 478
Steel, G. E., 805
Steel, J. K., 493, 503
Steele, C. C., 871
Steele, G. J., 42
Steenbeck, M., 52
Steenbock, H., 780, 784, 785, 788-791, 793, 801, 802, 805, 813-815, 822, 824, 827, 829-831, 836, 837, 839, 840, 846, 853, 855
Stefan, 15-17
Steiger, R. E., 502, 674
Steigerwald, C., 259
Steigmann, A., 260, 629, 632, 804
Stein, C. P. 275
Stein, G., 805
Stein, H. B., 781
Stein, J. G., 660
Stein, N. O., 298, 307, 329, 330
Steinbach, M. M., 773, 824
Steinberg, A., 657
Steinberger, F. K., 343, 483
Steiner, A. B., 393
Steiner, P. E., 748
Steiner, W., 156-158, 230, 272, 279, 282, 295, 380
Steinmetz, C. P., 46
Stenger, E., 97, 182
Stenström, M., 479
Stenstrom, W., 803
Stephen, D., 397
Stephen, W. E., 869
Stephens, F. L., 890
Stephens, H., 775
Stephens, H. C., 829
Stephens, H. L., 883
Stephenson, A., 464
Sterges, A. J., 350
Stern, A., 377
Stern, B. E., 855
Stern, E., 597
Stern, H. J., 882
Stern, K. G., 685, 851, 859
Stern, O., 214, 272, 287
Sterzel, S. E., 358
Stevens, D. S., 160
Stevens, F. A., 727
Stevens, N. M., 718
Stevenson, M. M., 819
Stewart, J. Q., 2
Stewart, K., 333
Stewart, T. D., 529, 534, 535
Stewart, W. D., 889
Stieger, G., 306, 310, 312, 536
Stiehl, K., 522
Stiemens, H., 754
Stiles, W., 866, 874
Still, E. U., 822
Stimson, F. J., 42
Stiven, D., 753
Stix, E., 518, 522
Stobbe, H., 343, 385, 396, 410, 478, 483-485, 488, 489-491, 493, 517
Stock, A., 62, 124, 359
Stock, L. W., 379
Stockbarger, D. C., 34, 97, 111, 174, 176, 177, 789
Stockelbach, F. E., 183, 743
Stockhausen, K., 762
Stockmann, H., 413
Stoeckly, J. J., 650
Stoermer, R., 413, 438, 447, 448, 452, 455, 456, 480-483, 488, 882
Stokes, G., 6, 207
Stokes, J., Jr., 836, 842
Stoklasa, J., 715, 868, 888
Stoll, A., 867, 871, 876, 878
Stoll, B., 101
Stoll, W., 810
Stolt, H., 48
Stone, F. M., 670
Stone, J. F. S., 547, 883
Stora, C., 269
Storch, H. H., 318
Storey, H. H., 860
Strachan, E. K., 153
Strachow, N. van, 344
Strain, D. E., 584
Strain, H. H., 888
Strangeways, T. S. P., 708
Strating, J., 413
Straus, F., 478
Strayer, J. W., 818, 823
Strebel, A., 516
Streck, E., 385
Streeter, L. R., 890
Strepetov, N. P., 494
Strickland, R. F., 143
Strieter, O. G., 661
Stringfield, O. L., 841
Strömberg, R., 376
Strong, J., 96
Strott, A., 888
Struck, H. C., 742, 785, 819, 824
Struck, H. D., 822
Strukov, I., 497, 550
Stuart, H. A., 257
Stuart, P. A., 809
Stuckardt, K., 182, 272, 274, 275
Studienges, für Wirtschaft und Industrie, 139
Studnitz, G. von, 857
Stueckelberg, E. C. G., 163, 293
Stücklen, H., 155, 394
Stuff, F., 45
Stuhlman, O., Jr., 36
Sturrock, W., 144, 147
Stutz, G. F. A., 556, 568-571, 583, 585, 587
Stutzke, S., 858

Style, D. W. G., 190, 248, 250, 252, 282, 304, 399
Subramonium, B. R., 546
Sucharavskii, M., 472
Suciu, M., 626
Suckfüll, E., 805
Sudborough, J. J., 467
Süllmann, H., 852
Süs, O., 872
Sugie, J., 179
Sugie, S., 168
Sugihara, N., 742
Suguiera, J., 236
Suguira, Y., 50, 149, 163
Suhrmann, R., 131
Suida, H., 467, 468, 473, 481, 515
Suirkin, Y., 254
Sullivan, W. N., 659
Sumi, M., 803, 807
Summerfeldt, C., 824
Sunder, C., 574
Sundhoff, D., 314, 533
Sung, T.-T., 682
Sunzeri, G., 865
Super, L. P., 706
Supniewski, J. V., 860
Supplee, G. C., 813, 814, 839, 841-844, 846, 848, 852
Surányi, G., 709, 750
Sure, B., 851
Surie, E., 795
Suryanarayana, K., 343, 348
Sushkevitch, T., 309
Sutherland, E. C., 723
Suzuki, K., 759
Suzuki, M., 505
Suzuki, S., 172
Suzuki, T., 183, 857
Svedberg, T., 64, 181, 379, 386, 670
Sventitskii, N. S., 50
Sveshnikov, B. Y., 262, 335
Sveshnikova, N. P., 837
Sviridova, T. A., 706
Swain, G., 810
Swann, W. F. G., 713
Sward, G. G., 580, 581
Swartz, O., 710
Swensson, T., 545
Swingle, W. W., 755
Swings, P., 168
Sykes, J. F., 822
Sylvania Corporation, 561, 562
Sylvester, N. D., 559, 560, 831
Szakáll, A., 746
Szalay, S., 434, 435
Szarvasy, E., 530
Szegö, L., 624
Szendrö, P., 673, 678
Szigetti, B., 271
Szilard, A., 624
Szillard, 97
Szörenyi, E., 863
Szörenyi, E. T., 860
Szulc, N., 57
Szüts, A., 860

Tabern, D. L., 832
Taboury, M.-F., 391
Täufel, K., 432, 553
Tafel, J., 703
Taher, N. A., 428
Takagi, T., 188
Takahashi, T., 111
Takahashi, Y., 163
Takamiya, E., 804
Takata, R., 790
Takayama, T., 683
Takebe, T., 106
Takei, M., 619
Taketomi, N., 434
Talen, H. W., 603
Talmud, D. L., 334, 465
Tamiya, H., 630
Tampier, L., 423
Tamura, A., 756
Tamura, M., 289
Tanaka, K., 630
Tanaka, T., 156
Tanaka, Y., 608
Tănăsecu, E., 478
Tănăsecu, H., 472
Tănăsecu, I., 472, 475, 478, 482, 490, 516, 626
Tanberg, R., 48, 49, 119
Tandon, S. P., 350
Tang, P. S., 717
Tang, T.-H., 682
Tangl, H., 750
Tanino, F., 756
Tanner, F. W., 710
Tanner, R. R., 648
Tannigen, F. C., 621
Tanret, G., 795, 823, 832, 434, 436
Tappan, C., 60
Tappeiner, H. v., 344, 860
Tartakowsky, P., 375
Tasaki, T., 476, 487
Tataranu, F., 757
Tataranu, I., 747
Tatnall, R., 49
Tatum, W. W., 550
Taub, A., 657
Taube, H., 348
Tauss, J., 655
Tautini, E., 742
Taverne, N., 573
Tawde, N. R., 364
Taylor, A., 60
Taylor, A. H., 147, 179, 181, 642, 738
Taylor, A. M., 383
Taylor, A. W. C., 272, 275
Taylor, B. S., 610
Taylor, E. M., 165
Taylor, H. A., 459, 460, 504
Taylor, H. S., 86, 125, 150, 156, 212, 257-259, 284, 301, 303, 310, 313, 317, 319-323, 340, 394, 397, 403, 406-408, 410, 414, 415, 422, 427, 439, 458, 464, 488, 683
Taylor, J. S., 51, 97
Taylor, M. W., 814, 856
Taylor, N. B., 818, 822
Taylor, W., 182, 246
Taylor, W. C., 166
Tchakhotine, S., 704, 717
Teagarden, E. J., Jr., 523, 865
Tear, J. D., 6
Tede, K., 363, 368
Teele, R. P., 193
Teft, R., 391
Teichler, G., 674
Teichmann, C. F., 531
Teindl-Czech, L., 709
Teller, E., 236, 240, 244, 330, 331, 375
Templin, V. M., 822, 824
Tenchio, F., 740
Tennant, R., 681
Teplov, I., 750, 865
Terata, B., 689
Terenin, A., 190, 231, 238, 240, 241, 263, 345, 402, 438, 439, 464
Tern, R., 554
Terrien, J., 382
Terroine, E. F., 681
Testi, G., 620
Tetzner, E., 756
Teves, M. P., 241
Thacker, E. A., 826
Thalman, R. R., 786
Thatcher, L., 822
Thayer, R. N., 142
Thayer, S. A., 856
Thee, W. C., 663
Theiler, A., 783
Theiss, E. R., 651
Theobalt, Mlle., 781
Theorell, H., 670, 688, 853, 857
Thermal Syndicate, 147, 151
Thibaut, J., 8
Thiele, H., 299, 308, 333, 693, 698
Thiele, W., 810
Thiessen, P. A., 389
Thoenes, F., 822
Thomas, A., 109
Thomas, B. H., 813, 822, 830, 835, 837-839,
Thomas, J., 687
Thomas, P. H., 77
Thompson, A., 76
Thompson, E. G., 618
Thompson, H. E., 804
Thompson, H. W., 333, 334, 423, 425, 426, 460, 461, 464, 854
Thompson, L., 727
Thompson, W. P., 77
Thompson, W. R., 681, 683, 765
Thomson, D. L., 819
Thomson, E., 151
Thomson, G. P., 11
Thomson, J., 32
Thomson, J. C., 564
Thomson, J. J., 269, 287
Thomson, R. F., 550
Thomson Research Laboratory, 151
Thon, N., 281, 287
Thoraeus, R., 8
Thornton, W. N., 95
Thorpe, J. F., 541
Thouret, W., 94
Thovert, J., 381
Thovert, J. F., 381
Thunberg, T., 877
Tian, A., 73, 206, 299, 339
Tichalskaya, V. V., 849
Tiede, E., 366, 793
Tiedemann, W., 546
Tietz, E. L., 422, 423
Tietze, E., 183
Tietze, W., 109
Tiggelen, A. van, 320
Tillisch, H. C. E., 827
Tingey, H. C., 156, 230, 272, 275
Tingley, S. L., 655
Tisdall, F. F., 170, 782, 824, 830, 837
Titeica, R., 511
Titoff, A., 357
Titov, A. I., 470
Tittel, H., 209
Tittsler, R. P., 704
Titus, H. W., 787, 814
Titus, R. W., 787 854
Tival, H., 727
Tixier, G., 798, 829, 832
Tkachev, A. D., 560, 573
Tobey, J. A., 835
Tobin, E., 492
Tobiska, J. W., 856
Toczyski, T., 754
Todd, C., 860
Todd, T. W., 818
Töpelmann, H., 792
Toepfer, K., 410
Török, L., 741
Tognoni, C. A., 587
Togo, S., 94
Tokumitu, Y., 749
Toldte, W., 580, 581

Tollman, J. P., 51
Tolloczko, S., 393, 394, 526
Tolman, R. C., 209, 210, 247, 249, 250
Tompkins, H. K., 530
Tompkins, R. G., 722
Toni, G. de, 732, 754
Tonks, L., 81, 83, 84, 94
Tonnet, J., 756
Tonney, F. O., 835
Topchiev, A. V., 470, 521
Topley, W., 776
Toporetz, A., 378
Toriyama, Y., 40
Tottingham, W. E., 883, 887, 888
Toul, F., 415
Townend, R. V., 306
Toy, F. C., 377, 379
Toyabe, Y., 611
Toyama, J., 686
Toyoda, G., 749
Tracy, G. P., 523
Trajtenberg, S., 744
Tramm, H., 286, 308
Tranin, S., 722
Transeau, E. N., 866
Trautmann, G., 795, 796, 813
Trautz, M., 209, 255, 274, 316, 331, 332
Trebler, H. A., 840
Treibs, W., 515, 516
Trehana, F. C., 870
Trehin, R., 343
Trelease, S. F., 882
Trevorrow, V. E., 824
Trevy, P., 592
Tricault, G., 823
Triebold, H. O., 840
Trifonoff, A., 288
Trifonov, N., 444
Trillat, J. J., 376
Trischmann, H., 484
Tristan, F., 178
Trivedi, H., 275, 281
Trivédi, R., 482
Trivelli, A. P. H., 376, 379, 380
Trolliet, A. L., 587
Trotman, S. R., 188, 621
Trotskii, V. L., 706
Trufanov, A. V., 832
Truffault, R., 532
Tsai, L. S., 456
Tschentke, H. L., 572
Tshubarov, R., 240
Tsirg, I., 93
Tsi-Zé, N., 297
Tsuchida, R., 368
Tsuge, H., 849
Tsukamoto, K., 338
Tuchel, H., 346
Tuenter, J. P. A., 346
Türkenburg, F. R. von, 73
Tuffail-Malkana, M., 522
Tully, W. C., 814
T'ung, T., 860, 865
Tupholme, C. H. S., 624
Turek, O., 472
Turner, A. A., 720
Turner, E. E., 546
Turner, H., 609
Turner, J. S., 644
Turner, L. A., 24, 83, 231, 243, 257, 273, 275
Turner, W. E. S., 167, 169, 171, 173
Tweedy, W. R., 754
Twyman, F., 271, 853
Tyndall, E. P. T., 155
Tyndall, J., 205
Tzoni, H., 817

Uchimura, T., 760
Ueda, H., 671
Uehara, K., 683
Ugo, A., 734, 766
Uhlenbeck, G. E., 25
Uhlmann, E., 734, 738
Ulbrich, W., 75
Umesawa, H., 621
Ungar G., 383
Unger, L. J. 778, 779, 783
Unger, W., 287, 288
Universal Oil Products Co., 652
Unsöld, A., 94
Untersuchungs und Forschungs Laboratorium für Lacke und Farben, 589
Uppal, H. L., 249, 253, 486, 540
Uraki, J., 817
Uraki, Z., 670
Urbach, E., 743
Urbach, F., 861
Urbain, E., 74, 359, 394, 514, 539
Urban, 42
Urbán, F., 741
Urban, F. F., 672
Urban, O., 883
Urbanczyk. W., 431, 432
Ure, W., 210
Urey, H. C., 25, 158, 159, 210, 228, 243, 303, 307, 327, 339
Urmston, J., 280
Urmston, J. W., 536
Ursprung, A., 715, 873
Urushibara, Y., 817
Ushakov, S. N., 591
Usher, F. L., 868
Utaka, S., 550
U. V. Generator Corp., 58

Vacek, T., 688
Vadimov, M., 720
Vadimov, V., 837
Vagedes, H., 721
Vahle, W., 101, 737-739
Vahlquist, B., 822
Vaidya, B. K., 188, 453, 456, 522
Vaidya, B. M., 484, 488
Vail, C. E., 856
Vaillant, P., 368
Valdiguié, A., 407, 432, 525
Valenta, E., 168
Valentin, H., 732, 885
Valyashko, N. A., 479
Vaney, G. M. de, 787
Van den Berg, L. M., 396
Van der Hulst, 565
Van der Linden, T., 543, 544, 547
Van der Lingen, 44, 693, 694, 698
Van de Walle, H., 412
Van der Ziel, A., 447
Van Dyk, A., 409, 410
Van Eekelen, M., 817
Van Houten Co., 831
Van Itallie, P. H., 743
Van Leersum, E. C., 831
Van Niel, C. B., 881
Van Recsey, E., 829
Van Recsey, N., 81, 829
Van Sant, R. H., 81, 829
Vanselow, W., 377 382
Van Stolk, D., 797
Van't Hoff, 206
Van Veen, A. G., 873
Van Vleck, J. H., 19
Van Voorhis, C. C., 82, 83, 293
Van Wijk, A., 115, 799, 801, 803, 805-808, 815, 829, 833
Van Wyk, A., 171
Van Zuydewijn, E. de R., 413
Varadanam, C. I., 259
Varahalu, K., 268, 367
Varalalu, T., 367
Varela Fuentes, B., 822
Vareton, E., 869
Vargin, V. V., 171
Varley, W. M., 179
Varma, P. S., 546, 550
Varshaver, G. S., 747
Vartanyan, A. T., 259
Vasarhelyi, J., 744
Vashist, S. D., 617
Vasilief-Sinzova, A., 369
Vassy, E., 152, 193, 297
Vatter, H., 83, 93
Vaughan, W. E., 295
Vacchiotti, L., 468, 470, 496
Vedder, A., 756
Vellinger, E., 651, 654
Velluz, L., 508, 511
Velluz, Mme., 508
Venar, Y., 818
Vendor, A., 638
Venkataramaiah, Y., 284
Verda, D. J., 689
Verdollin, J., 689
Vereinigte Chemische Fabriken Kreidl Heller & Co., 508
Verhoeff, F. H., 763
Vermes, M., 709, 750
Vermeulen, D., 48, 52, 877
Vernon, A. A., 410, 488
Veronita, M., 708
Verreries de Goetzenbruck, 167
Veselkin, N. V., 849
Vesper, H. G., 532
Viale, G., 260, 733, 849
Vickery, H. B., 884
Victor, E., 346
Vieweg, A., 42
Vignard, 784
Vignon, L., 613
Viktorin, O., 479
Vila, A., 580
Vilenkin, M., 832
Villard, 7
Villard, P., 209
Villars, D. S., 182, 190, 224, 228, 352-354, 456
Villemaine, F., 370
Vincent, J. H., 120
Vines, H., 755
Virasoro, E., 684
Virden, C. J., 484
Virtanen, A. I., 849
Visser, G. H., 236, 238, 476
Vita, N., 254, 255, 344, 441, 443, 485
Vitalite Co., 173
Viterbe, E., 364
Vitoria, A. P., 431
Vlès F., 441, 651, 670, 734, 764, 766
Vodar, B., 349
Voege, W., 96
Voelker, 151
Voet, J., 712
Vogel, 381
Vogel, H., 435
Vogele, A. C., 888
Vogeler, L., 722
Vogels, H., 264, 352
Vogler, H., 376
Vogt, K., 273
Voigt, J., 387
Vöitz, W., 836
Volbert, F., 271, 351, 495, 564, 565
Völker, H., 744, 745
Volkringer, H., 94, 412, 670
Vollgraff, J. A., 473, 513, 514

Vollmann, H., 586
Vollmer, H., 783
Volman, D., 420
Volmar, 246, 402, 441, 448, 450, 454, 538
Volmer, M., 58, 60, 209, 214, 272, 287, 376, 505
Völtz, W., 790
Volz, K., 643
Vore, H. B. de, 592
Vorländer, D., 193, 485, 492, 869
Vorozhtzov, N. N., 501
Vorster, D., 860
Voss, A., 411
Voznava, A., 837
Vranek, J., 368
Vries, H. de, 361

Wachholtz, F., 454, 455
Wäckerlin, E., 443
Waddell, J., 814, 834, 838
Wadhera, M. L., 434
Wadsworth, A., 690
Waele, A. de, 456, 589
Waentig, P., 613
Wagner, C., 207, 297, 306, 311, 313
Wagner, H., 577, 582-584
Wagner-Jauregg, T., 314, 851
Waguet, P., 111
Wahl, A., 617, 638
Wahl, H., 381
Wahlberg, H. E., 618
Wait, R., 817
Wakeham, C., 523
Wakeman A. J., 884
Wakkie, J. G., 871
Waksman, S. A., 351
Wald, G., 857-859
Waldbauer, L., 216
Waldie, A. T., 317
Walker, O. J., 360, 431, 440
Walker, P. H., 579, 581
Walker, R. D., 381
Walker, T. T., 823
Walkoff, E., 820
Wall, E. J., 556
Wallace, J., 306, 307
Wallach, O., 473
Waller, M. D., 734, 741
Wallis, G., 835
Wallraff, A., 32
Walls, H. J., 182
Walsh, J. F., 173
Walter, C., 555
Walter, E., 467, 796, 797
Walter, H., 558
Walter, P., 580, 605
Walters, E., 254, 446
Walters, F. M., Jr., 50
Walther, H., 662
Walther, R. v., 493
Walther, T., 387
Waltner, K., 791
Walton, J. H., 365
Wansbrough-Jones, O. H., 356, 437, 438
Waran, H. P., 77
Warburg, E., 43, 44, 210-212, 214, 215, 246, 272-275, 288, 292, 294, 297, 318, 321, 342, 352, 353, 355, 453
Warburg, O., 333, 687, 688, 732, 853, 874-876, 879
Ward, H. K., 750
Ward, H. M., 692
Warde, F. M., 165
Wardle, G. C., 636
Warga, M. E., 98, 99, 201
Warkany, J., 818
Warming, E., 310, 313
Warmoltz, N., 131
Warmuth, K., 52
Warren, D., 273
Wartenberg, H. v., 249, 349
Warweg, E., 819
Washburn, M., 209
Washburn, R. G., 841
Washburne, R. N., 210
Wasicky, R., 556
Wassermann, A., 453
Wassiljewa, A., 281, 387
Wassink, E. C., 877, 881
Wasteneys, H., 680, 683, 684
Wastl, H., 760
Watanabe, A., 260, 882
Watenpaugh, J. T., 818
Waterman, H. I., 411
Watkins, J. S., 289
Watson, H. E., 367, 467, 468, 474, 522
Watson, H. L., 151, 818
Watson, M. B., 848
Watson, W. H., 161
Watson, W. W., 273, 330
Watta, H. G., 417, 418, 426, 474
Watters, B. D., 116
Watteville, C. de, 35
Wawilow, S. J., 262
Way, 66
Wearham, J., 847
Webb, C. N., 421
Webb, D. A., 64
Webb, J. H., 271, 374, 376, 377, 381
Webb, W. W., 347, 442
Weber, A. E., 507
Weber, K., 263, 351, 445, 522, 631, 871
Weber, P., 526
Webster, A., 102
Webster, H. G., 334
Webster, S. B., 135
Webster, T. A., 695, 788, 792, 794-798, 800, 801, 803-806, 821, 822, 853, 867-869, 882
Weckel, K. G., 829, 835, 840, 841, 845
Weedon, H. W., 555
Weegmann, E., 331
Weger, M., 517
Wegmann, T., 679
Wegscheider, R., 251, 475
Wehnelt, A., 131, 133
Weichmann, H. K., 183
Weickart, F., 646
Weidenbaum, B., 529, 534
Weidert, F., 168, 178
Weidlich, G., 807, 821, 832
Weigel, O., 359
Weigert, F., 69-71, 216, 266, 282, 284, 286, 297, 314, 341, 379, 383, 474, 475, 504, 505, 523, 524, 857, 877
Weightman, H. E., 607
Weingeroff, M. A., 156
Weinhouse, S., 817
Weinstein, I., 700, 701, 716
Weinstock, M., 773, 779-781, 785, 788, 789, 791-794, 803, 836
Weisbecker, H 860
Weisberg, S. M., 852
Weiser, H. B., 385
Weiss, H., 368
Weiss, J., 261, 263, 264, 360, 370, 463, 630, 631, 871, 872, 881
Weizel, W., 83, 163, 228, 833
Weizmann, C., 403, 671, 672
Welch, H., 690, 720, 725
Welch, J. W., 826
Weld, C. B., 818, 822
Weld, H. W., 172
Welge, H. J., 321
Wellburn, E. R., 404
Wellmann, M., 172, 380
Wells, A. A., 558, 568
Wells, D. A., 68
Wells, M. W., 731
Wells, W. F., 712, 731
Wels, P., 676-678
Welsh, J. H., 865
Weltner, M., 670, 853
Wendt, B., 562
Wendt, G. von, 817
Wendt, G. L., 284
Wenger, W., 757
Wenig, K., 676
Wenner, R. R., 321, 323
Werder, F. von, 804, 807, 808, 814, 816
Werle, E., 691
Werner, E. A., 358
Werner, G., 648
Werner, H., 553, 559
Werner, O., 867
Werschen-Weisserfeldser Braunkohlen A.-G., 653
Werthan, S., 578
Wessely, F., 515
West, D. L., 179
West, E. S., 867
West, H. D., 541
West, H. L., 539
West, W., 244, 260, 262, 280, 336, 397, 398
Westbrook, A., 715, 885
Westbrook, M. A., 715
Westhaver, J. W., 31, 327
Westin, G., 849
Westinghouse Electric and Manufacturing Co., 74, 724
Westinghouse Lamp Co., 139, 140
Westphal, K., 804
Westra, J. J., 689
Weyde, E., 105, 628, 629
Weygand, F., 852
Weyl, T., 183
Wheatstone, C., 66
Whipple, D. V., 836, 842
Whitaker, M. D., 36
White, B. B., 585
White, H. L., 25
White, P. C., 545, 550
Whitehead, H. R., 762
Whitley, E., 881, 882
Whitmore, W. B., 645
Whitnah, C. H., 852
Whittaker, C. M., 624
Whittier, C. C., 832
Wichart, 472
Wickman, P. A., 562
Wickwire, G. C., 752, 763
Wiebe, R., 217
Wiedemer, C., 748, 774
Wiedermann, G., 92
Wiegand, C., 183, 743
Wiegand, K., 137, 142, 840
Wiegel, E., 388
Wieland, 827
Wieland, H., 444, 490
Wieland, K., 330
Wien, W., 15-17
Wienands, A., 493
Wiener, C., 785
Wiener, H., 703
Wiersma, C., 764
Wierzuchowska, J., 670
Wiesler, K., 425
Wiesner, R., 698
Wietzel, G., 439
Wietzel, R., 439

Wiggam, D. R., 591
Wightman, E. P., 379
Wiig, E. O., 318-322, 399, 536, 537
Wijnand, P. C., 597
Wilbur, P., 497
Wilcox, D. E., 814, 838
Wild, G. L. E., 431, 440
Wild, W., 397, 427
Wilder, R. M., 788
Wilder, W., 838
Wildermann, M., 206, 311
Wilhelm, H. A., 64
Wilke, P., 643
Wilkie, J. B., 853
Wilkins, L., 784, 785
Willard, J., 535
Willemart, A., 508, 509
Willenberg, H., 35
Willi, E., 480
Williams, C. H. M., 824
Williams, D. M., 488
Williams, E. G., 344
Williams, I., 602
Williams, J. G., 615
Williams, J. J., 581
Williams, J. M., 447
Williams, R. R., 479, 480, 851
Williams, T. G., 449, 516
Williamson, R., 497
Williamson, W. O., 386
Willimott, S. G., 785, 854
Willis, H. S., 772
Wilmanns, G., 183
Wilsing, J., 152
Wilson, A. H., 372
Wilson, D. A., 104, 444
Wilson, E. D., 98, 155
Wilson, F. J., 490, 491, 493, 494
Wilson, G. H., 142
Wilson, J. H., 587
Wilson, L. D., 123
Wilson, L. T., 838
Wilson, W., 51, 377
Willstätter, R., 863, 867, 871, 875, 876, 878, 879
Wimmer, C., 556
Winans, J. G., 36, 95, 163
Winchester, 194, 195
Windaus, A., 792, 795, 796, 801, 803-810, 812, 813, 816, 821, 832, 834, 862
Winderlich, R., 124
Wingchen, H., 476
Wingfoot Corporation, 612
Winkler, C. A., 427
Winn, A. G., 446
Winninghoff, W. J., 77
Winship, W. W., 151
Winter, E., 283
Winterstein, A., 854, 856
Wintersteiner, O., 851
Winther, C., 105, 107, 173, 179, 182, 210, 253, 255, 270, 305, 344, 361, 367, 370, 441, 444, 448
Winthrop Chemical Co., 659, 833, 834
Winzor, F. L., 502
Wirick, A. M., 815, 822, 831, 855
Wirth, C., 653
Wisconsin Alumni Research Foundation, 827
Wislicenus, W., 454, 493
Wiskott, A., 821, 822
Withrow, L., 663
Withrow, R., 184, 186, 726, 828
Witmer, E., 217
Witt, O. N., 626
Wittgenstein, A., 764
Wittka, F., 563
Wittstein, G., 205
Wix, A., 660
Wlodek, J., 871
Wobbe, D. E., 441
Wöber, A., 890
Wodlinger, M. H., 847
Woelffer, E. A., 838
Woerner, H. B., 60
Wohl, K., 879-881
Wohl, Mlle., 495
Wohlgemuth, J., 742, 863
Wokes, F., 785, 854
Wolf, 386
Wolf, C. E. de, 885
Wolf, E., 460
Wolf, G., 626
Wolf, J., 169, 436
Wolf, K., 693, 698
Wolf, K. L., 163, 416, 425, 467
Wolf, L., 124
Wolf, M., 876
Wolfers, F., 366
Wolff, H., 176, 330, 576, 586, 587, 589
Wolff, K., 314, 532
Wollaston, W., 6
Wollmann, E., 588
Wollner, F., 171
Wollner, R., 171
Wölpert, K., 849
Wolter, E., 806
Woo, S. C., 414
Wood, A. R., 176
Wood, B. G., 514
Wood, B. J., 542
Wood, H. P., 663
Wood, J. G., 874
Wood, R. W., 7, 86, 109, 178, 190, 257, 467
Wood, W. C., 273, 336, 345
Woodhouse, J. C., 524
Woodroffe, D., 651
Woodrow, J. W., 556, 709, 853, 854
Woods, G. M., 487
Woods, H. J., 679
Woog, P., 555, 656
Wormall, A., 757, 758
Wörner, A., 830
Wotherspoon, R., 658
Wrede, B., 155
Wrede, F., 673
Wright, P., 115, 165
Wright, R., 273
Wright, S., 803
Wright, W. H., 718
Wright, W. L., 620
Wulf, 9
Wulf, O. R., 193, 294-296, 327
Wulf, T., 35
Wulff, P., 364
Wunderlich, W., 816
Wurmser, R., 213, 339, 425, 435, 874, 881, 882
Würth, K., 568, 576
Wurzinger, S., 820
Wyat, L., 825
Wyckoff, R. W. G., 705-708
Wyman, E. T., 174, 782, 789, 835, 838, 839
Wynd, F. L., 688, 710, 888, 889
Wyneken, I., 155
Wyrobek, O., 478, 479, 482
Wyszewianski, L., 617

Yajnik, N. A., 249, 253, 390, 434 486, 540, 870
Yakota, S., 751
Yakushiji, E., 877
Yamafuji, K., 685
Yamagishi, T., 851
Yamaguchi, T., 619
Yamamoto, E., 625
Yamamoto, R., 851
Yamanaka, G., 757
Yamanaka, T., 495
Yamashiki, H., 681
Yamashita, S., 553, 625
Yamazaki, T., 607
Yampolskii, B., 179
Yanagihashi, T., 584
Yankin, G. M., 31
Yao, Y. T., 82
Yarnold, E. T., 404
Yeremenkow, N. P., 794
Yoda, G., 506
Yoder, L., 794, 804, 813
Yokayama, K., 790
Yoshine, S., 745
Yoshitomi, M., 818
Young, C. H., 189
Young, F. E., 855
Young, F. G., 809
Young, K. W., 250, 443, 446
Young, T., 3, 4, 6
Yovanovitch, A., 745

Zadoo, V. D., 390
Zaepffel, H., 748
Zagulin, A. V., 291
Zahn, R., 648
Zahour, R. L., 179
Zaidan-Hojin Aoyagi Kenkyisho, 143
Zaidan Hojin Rikagaku Kenkyujo, 183
Zakowski, J., 388
Zamfirescu, G., 460
Zanetti, G., 468, 470, 496
Zavadovskii, M., 837
Zchodro, N., 632
Zdobnicky, W., 868
Zé, N. T., 156, 157, 163
Zecher, G., 139, 829, 832
Zehender, F., 852
Zeidler, G., 580, 587, 589
Zeile, K., 685
Zeise, H., 217
Zeiss, C., Co., 167
Zeiss, Ikon A.-G., 60
Zel'dovich, P. Y., 588
Zeller, H., 709
Zemansky, M. W., 92, 257
Zenghalis, C. D., 308
Zernik, F., 183
Zeyland, J., 823
Zeynek, R., 751
Zhalkovskii, B. G., 267
Zhukov, I., 411
Zhukova, A., 582
Zia, S. H., 860, 865
Ziegler, M. R., 792, 794, 830
Ziegler, W., 171, 172
Ziegler, Z., 865
Ziegler-Wellmann, M., 759
Ziersch, G., 626
Ziffer, F., 530
Zikes, H., 865
Zilg, W., 444
Zilva, S. S., 848, 854
Zimmer, K. G., 475
Zimmerli, A., 173
Zimmerman, A., 471
Zimmermann, W., 105, 628, 629, 833
Zinov'ev, A. A., 559
Zintl, E., 366, 624
Ziskin, M., 309

Zlatarov, A., 554
Zmanovskaya, L. I., 31
Zocher, H., 266, 383
Zolcinski, J., 350
Zondek, B., 689
Zouckermann, R., 37
Zschacke, F. H., 671
Zscheile, F. P., Jr., 271, 870
Zschimmer, E., 168
Zschoch, F., 483, 517
Zuber, K., 227
Zucker, T. F., 816, 824, 838
Zuckerstein, E., 755
Zueva, R. V., 588
Zuithoff, A. J., 413
Zurukzoglu, S., 792
Zussman, H., 858
Zwaardemaker, H., 513

Subject Index

Abscesses, 825
Absorption bands, and optical rotation, 266
  coefficient, 207, 271
  curve, 271
  of light, and dissociation, 227
  of light by gases, 179, 285
  of light, effects due to various wave-lengths, 208
  of light, laws, 206
  spectra (see Spectra)
Acamnine, 710
Accelerated tests (see Tests, accelerated weathering)
Accelerators, 252, 365, 648
  for rubber, 596, 598-601, 605, 610
Acceptors, 211, 863, 864, 871, 872
  in dye bleaching, 263, 264
Acenaphthene, 511
Acenaphthenequinone, 603
Acetal, 416, 709
Acetaldehyde, 452, 481, 595, 868
  absorption spectrum, 416, 418-420
  fluorescence, 419
  formation, 396, 397, 402, 422, 429, 431, 448, 449, 672, 676
  photoreactions, 417-423, 425
Acetaldehyde, dimethyl, 421
  hexahydrophenyl, 424, 473
  phenyl, 424, 473
  trimethyl, 421
Acetaldol, 425
Acetamide, 340, 438, 647
Acetanilide, 340, 438, 495, 657
Acetates, 377, 536, 681
Acetic acid, 184, 340, 418, 617
  absorption spectrum, 565
  chlorination, 540
  formation, 404, 422, 425, 428, 431, 441, 447, 449, 451, 514, 515
  photoreactions, 437, 438
Acetic acid, bromo, 451
  chloro, 249, 451, 452, 540, 594
  phenyl, 478
Acetic anhydride, 473, 540
Acetoacetic acid, 362
Acetoin, 421, 451
Acetol, 173, 518
Acetone, 340, 357, 362, 421, 433, 510, 514, 562
  absorption spectrum, 425-428
  and ethylene polymerization, 408
  and lens proteins, 763
  dicarboxylic acid, 362
  dihydroxy, 339, 404, 428, 432
  dissociation, 244
  formation, 396, 402, 404, 429, 431, 450
  in detection of pyridine, 521
  methylene blue reaction, 102, 103, 105
  nitrosoisopropyl, 461
  oxidation, 425
  photolysis, 397, 420, 425-428
  reaction with butanol, 403
  reaction with terpene alcohols, 514
  sensitizer of ether photolysis, 405
Acetonuria, 752
Acetophenone, 340, 344, 430, 477
  anisal, 478
  amino, 498
  benzaldehyde condensation product, 490
  carboxylic acid, 478
  dimethylamino, 629
  pinacol, 403
  reaction with alcohols, 403
Acetylacetone, 431, 465
Acetylbenzoyl peroxide, 480
Acetyl bromide, 440
Acetylbromoindazole, 743
Acetylcarbazole, 743
Acetylcellulose, 173, 587, 591
Acetyl chloride, 440, 465, 534, 535, 540
Acetylchloroaminobenzene, 496, 497
Acetylcoumaric acid, 488
Acetylene, 393, 407, 415, 457, 537
  absorption spectrum, 414
  behavior in electrodeless discharge, 36
  bromination, 537, 538
  chlorination, 537
  deutero, polymerization, 415
  divinyl, 415
  formation, 62, 399, 400, 406, 424, 514
  oxidation, 414, 415
  phenyl, 538
  polymerization, 414, 415
Acetyl halides, photolysis, 440
Acetyl peroxide, 411, 431, 440
Acetylphenyltriazine, 647
Acetyl radical, 421, 427
Acetylsalicylic acid, 436
Acetyltoluene, 547
Acheson graphite, 64
Acid anhydrides, 410, 437
  chlorides, 437
  dyes, fading, 635, 636, 642, 644
Acidosis, 753, 754
Acids, aliphatic, 393, 437
  aromatic, 480-488, 600
  fatty, 553
  formation in gasolines, 653, 654
  halogenated, 451, 452
  in fermentation, 709
  in wine, 660
  organic, 437-456, 648
  polymerization inhibitors, 410
Acne, 742, 769
Aconite, tincture, 658
Aconitic acid methyl esters, 456
Acraldehyde, 435
Acridine, 509, 860, 862
  dyes, 640, 712
  phenyl, 509
Acridone, 507
Acrolein, 423-425, 669
Acrose, 402
Acrylic acids, 454, 456, 491
  ester polymers, 456, 584
Acryloid, 172
Actinometers, 96, 102-105, 202, 285, 341, 369, 400, 418, 433, 443, 452, 459, 600, 653, 656, 771
Action, 18
Activated molecules, 215, 216, 260-262
Activation energy, 207, 209, 210, 245-247, 250
  chlorine-sensitized oxidation of hydrogen, 289
  conversion of ergosterol into vitamin D_2, 812
  deuterium-chlorine combination, 290
  hydrogen-bromine combination, 276-278
  hydrogen-chlorine combination, 289, 291
  phosgene formation, 313
  reaction of atomic chlorine and hydrogen, 283, 284
  reaction of hydrogen with hydroxyl, 305
  reaction of O and O_2, 300, 309
  reaction of O and CO, 309
Acyloin, 451
Adaptors, for therapeutic irradiation 62, 63
Additivity, of rates of photo- and thermal reactions, 248
Adenine, 699, 701, 710, 850, 851

Adrenaline, 433, 688, 747, 760, 761
Adsorption, of carbon monoxide on quartz, 309
  on irradiated crystals, 259
Aerosols, 464
After-effects, photochemical, 253, 486
Afterglow, dyes, 264
Aftervulcanization, 597
Agar-agar, 585, 693-695, 697, 714, 758
Agglutinin, 757-759, 775
Agglutinogens, 758
Air, absorption of ultraviolet rays, 7, 192-202
  effect on output of mercury arc, 113, 114, 116
  formation of ozone, 292
  ionization, 269, 662
  irradiated and blood pressure, 780
  irradiated and rickets, 733
  lines, in spark discharge, 41
  mass, 192, 197, 198
  sterilization, 728-731
"Aktivin," 498
Alanine, 671, 672
Alanylglycine, 436, 671
Albumin, 390, 706
  egg, 674-679, 691, 758, 759
  serum, 674-677, 862
Alcohol, allyl, 538
  amyl, 471
  benzyl, 340
  butyl, 538
  ethyl (see Ethanol)
  isopropyl (see Isopropanol)
  octyl, 658
  propyl, 538
  tribromoethyl, 658
  trinitrobenzyl, 472
Alcoholic beverages, 207, 660
Alcohols, 369, 393, 401-405, 442, 458, 507
  as inhibitors of oxidations, 314, 356, 357, 422
  as polymerization inhibitors, 410
  bleaching of ferric chloride, 361
  bromination, 538
  conversion to sugar, 870
  formation, 432, 438, 449, 526
  from gasoline, 657
  in fermentation, 709, 710
  in mercury nitrate photolysis, 353
  oxidation, 356, 357, 404, 405, 476, 477
  poly, and lithopone blackening, 385
  reaction with benzoquinone, 480
  reaction with halo-acids, 452
  reaction with ketones, 403, 404, 517
  reaction with methylene blue, 686
  reaction with quinine, 523
Aldehyde-ammonia, 605
Aldehyde-phenol resins, 584
Aldehydes, 248, 366, 393, 407, 424, 449, 464, 546, 547, 589, 727, 728
  absorption spectra, 415-417
  and aromatic thiohydrazides, 500
  and phenanthrene quinone, 482
  aromatic, 472-476
  as polymerization inhibitors, 410
  formation, 404, 415, 448, 450, 458, 461, 468, 517, 619, 653, 673
  from secretin, 689
  in carbohydrate photosynthesis, 867, 868, 870
  in fermentation, 709
  oxidation, 422, 423
  photoreactions, 416-425
  rancidity and, 561
  reactions with quinones, 474
  reduction to alcohols, 418
  unsaturated, 423-425
Aldol-α-naphthylamine, 603, 610
Aldoketones, 430
Aldoximes, 493, 494
"Aldur," 170, 172
Alexin, 759
Alfalfa, 790, 830, 856
Algae, 713, 714, 717, 874-876, 881-883
Alizanthrene Yellow, 616
Alizarin, 603, 632
  Cyanin Green G, 622
  pigments, 590
  red lake, 643
Alkali bromides, 343
  carbonate, 172
  cations, absorption spectra, 337
  chlorides, 343
  fluorides, 238
  halide crystals, 216, 265, 372, 373
  halides, absorption spectra, 238, 239, 338, 372, 373
  halides, dissociation, 237
  halides, photolyses, 342, 343
  hydrides, in crystals, 375
  metal atoms, in crystals, 373
  metal oxides, 168, 169, 171
  metals, in liquid ammonia, 349
  reserve, 773
  tungstates, 369
Alkalies, spectra, 23, 24
Alkaline earth cathodes, 131, 133, 135-138
  cations, absorption spectra, 337, 338
  halides, absorption spectra, 338
Alkaloids, 407, 410, 466, 522-525, 658, 660, 726, 791, 882, 883
Alkanes, 460
Alkyl halides, 395-401, 496
  nitrates, 352
  peroxides, 339
  radicals, 395, 398, 402
Alkylbutadiene sulfones, isomerization, 413
Alkylnaphthylamines, azo dyes from, 626
Alkylphenylanthracenes, 509
Alkyns, and thiocyanogen, 457
Allantoin, 622
Allen-Doisy test, 756
Allene, 415
Allium cepa, 882
Alloxan, 702
Alloxazines, 852, 853
Alloy, cadmium-tin, for arc, 149, 150
Allwörden reaction, 622
Allyl alcohol, 407, 538
  cellulose, 591
  chloride, 550
  isothiocyanate, 457
  thiourea, 863
Almond oil, 513, 743
Alopecia, 744
Alpha-particles, 35, 287, 354, 713
Alpine sunlamp, 132-135, 658, 740
Alum, in paper, 644
Alumina, 168, 171, 172, 176, 179, 350, 387, 583, 673
  gel, 264
Aluminum, 171, 172, 359
  amalgam, 401
  and fatty acids, 554
  corrosion, 661
  electrodes, 156, 157, 159
  in carbon arc, 55, 57, 59
  lines, 190, 239
  reflector, 147
  sols, 386
  spark, 38, 153-155, 292, 299
Aluminum carbonate, 869
  chloride, 410, 411, 532, 545, 817
  hydroxide, 390, 391, 869
  phosphate, 172
  resinate, 619
  soaps, 586
Alveolar carbon dioxide tension, 753, 754
Amalgams, 149, 150, 360
Amboceptors, 759
Ames, Iowa, solar radiation at, 202
Amide ion, 349
Amides, 349, 350, 438, 458
Amines, 458, 648
  and chlorophyll bleaching, 871
  and oxidation of dye leucobases, 627
  aromatic, 495-499, 501
  as fluorescence quenchers, 262
  as polymerization inhibitors, 410
  formation from malachite green, 869
  N-substituted, 496, 497
  sensitized oxidation, 458, 863
Aminoacetanilide, 497

Aminoacetophenone, 498
Amino-acids, 350, 411, 670-673, 882, 883
Aminoanthraquinones, 617
Aminoaryldisulfoxides, 493
Aminobenzaldehyde, 498
Aminobenzoic acids, 498, 500, 743
Aminodimethylaniline, 497
Aminodiphenylamine, 624
Aminoethylenes, 407
Aminofluorene, 511
Aminomethylenecamphor, 515
Aminonaphthalene sulfonic acids, 562
Aminonaphthol, 647
Aminonaphtholcarboxylic acids, diazo compounds, 648
Aminonaphtholsulfonic acids, 624, 646
1-Amino-8-(8-nitro-1-naphthylsulfonyl)-2-naphthol, 501
Aminophenols, 468, 469, 479, 496, 497, 500, 610, 648
Aminopiperidinobenzoyl-H-acid, 647
Aminopyridines, 519, 520
Amino radical, 304, 309, 319-321
Aminostilbenesulfonic acid, 624
Aminothiazole, 498
Ammonia, 187, 359, 523, 647, 650, 883
  absorption spectrum, 224, 317, 349, 458
  and chloroform chlorination, 533
  and irradiated cholesterol, 793
  and unsaturated compounds, 407, 455
  as photosensitizer, 259, 303, 304, 408
  deutero, 322
  dissociation, 303, 309
  fluorescence, 258, 317, 322
  formation, 318, 353, 358, 364, 457, 458, 469, 498, 511, 672-674, 676, 689, 863
  inhibitor of chloroform oxidation, 314
  liberation, 671, 684, 702, 703, 858
  nitrogen and textiles, 621, 623
  oxidation, 193, 259, 322, 350, 883
  photolysis, 194, 211, 259, 318-322, 349
  predissociation, 241, 317, 319-321
  reaction with carbon monoxide, 322, 458
  reaction with deuterium, 320
  salts, 172, 350, 351
  silver chloride complex, 349
Ammonium acetate, 438, 440
  azide, 323
  benzoate, 438
  carbonate, 176, 350
  chloride, 329, 350, 681
  chromate, 364
  citrate, 682
  cyanate, 459
  dichromate, 645
  hydroxide, 438, 471, 883
  molybdate, 363, 369
  nitrate, 176, 322, 883
  nitrite, 322, 351
  oxalate, 172, 444, 445, 631
  phosphates, 172, 176
  sulfate, 184, 350
  tartrate, 172
  thiocyanate, 347, 358
Amoebae, 716, 717
Amphileptus claparedei, microirradiation, 713
Amygdalin, 436
Amyl acetate, 531, 562
  alcohol, 404, 407, 462, 471, 526
  amine, 863
  nitrite, 205
Amylase, 681, 683, 756
Amylene, 407, 538
Amylopectin, 436
Analysis, fluorescence, 178, 663-665
  spectrographic, 662
Anaphylactic shock, 748, 757, 758
Anemias, 747, 748, 750, 774, 777
Anesthesia, by irradiated alcohols, 402
Angioma serpiginosum, 769
Ångstrom unit, 5
Anharmonic oscillators, 234, 235
Anhydro-sugars, 869
Anilides, 455
Aniline, 464, 469, 495-498
  aminodimethyl, 497
  black, 469, 495, 646
  benzoyl, 496
  diazo-compound, 500
  dimethyl, 497, 643
  dyes, 469, 643
  ethoxy derivatives, 498
  formation, 496, 673
  -furfural resins, 585
  green, 634
  hydrochloride, 519, 645, 646
  inhibitor of hydrogen peroxide photolysis, 340
  isodiazotate solution, 646, 647
  methoxy, 497, 498
  nitro, 495
  nitrodimethyl, 479
  nitrosodimethyl, 495, 497
  reactions, 438, 455, 456, 496
  salts of nitronaphthalenesulfonic acid, 646
Anilinoacetic acid, 682
Anils, phototropy, 481
Anions, absorption by, 337, 338
  organic, electron-affinity spectra, 438
Anisalacetophenone, 478
Anisaldehyde, 494
Anisidine, 659
Anisylcinnamic acid, derivatives, 483
Anisylidene hydrazones, 493
Annatto, 643
Anode, carbon, 74, 139
  glow, 30, 31
  grid for accelerating electrons, 139, 142
  iron, for mercury arc, 75
  molybdenum, 149
  processes in mercury arc, 81, 85
  thorium-layered, 156
  tungsten, 74, 78, 80
Antagonism, of radiations, 150, 744
Anthocyanins, 715, 890
Anthoxyl radical, 507
Anthracene, 382, 503-505, 511, 562, 592
  absorption spectrum, 503
  9-alkyl-10-phenyl, 509
  diaryl, 508, 510
  diradical, 505
  ethyl, 509
  fluorescence, 261, 262, 504
  in therapy, 862
  -like compounds, 468, 507
  methyl, 505, 509
  oil, 618
  oxidation, 508
  phenyl derivatives, 508
  polymerization, 205, 206, 253, 504, 505
  tolyl derivatives, 508
  Yellow, 616
Anthranol, 508
Anthrahydroquinol-α-carboxylic lactones, 507
Anthrahydroquinones, 507
Anthranilic acid, 672, 673
  and cotton, 617
Anthraquinones, and derivatives, 467-469, 474, 506, 507, 518, 521, 550
  and rubber oxidation, 603
  in therapy, 862
Anthrax bacillus, 692, 696, 706
Anthrone derivatives, 506, 508
Antibodies, 757-759, 825
Antigen-antibody reaction in skin, 742
Antigens, 758
Antimonious acids, 390
Antimony, 172
Antimony chlorides, 355, 359, 539, 545, 817, 853-855
  halides in polymerizations, 411
  lamp, 148
  oxide, 167, 168, 359
  sulfide, 389-391, 610
  tartrate, 359
  triphenyl, 592
Antioxidants, 262, 548, 593-596, 600, 602, 603, 608, 621
Antisera, 691, 704, 756
Antisheep hemolysins, 758

Antithrombin, 825
Antitryptic activity, of serum, 757
Antityphoid substance, 757
Antiurease, 684
Apomorphine hydrochloride, 522, 726
Apozymase, 686
Apparatus, for dye testing, 638, 640
  for irradiating hides, 650
  for irradiating liquids, 184, 185, 829, 832
  for milk irradiation, 840-846
  for ozone formation, 292, 293
  for paint testing, 575, 576, 578-581, 586, 587
  for rubber testing, 605, 606
  high-frequency, 136
Apples, 890, 891
Applicators, for therapy, 62, 63, 770
Arabinose, 432, 433, 883
Arbacia, 717, 764
Arbutin, 436, 736
Arcs, aluminum, 227
  anode function, 47
  as photochemical sources, 50
  beryllium, 50
  cadmium, 48, 147-150, 231
  carbon (see Carbon arc)
  cathode processes, 31, 32, 47, 48
  copper, 47, 48
  definition, 30
  enclosed vapor, 65-95
  for decomposing hydrocarbons, 62
  for 3650 A., 179
  gold, 50
  iron, 46, 47, 49, 50, 102, 693
  low voltage, 190
  mercury (see Mercury arc)
  metallic, 46, 147-151
  nickel, 48, 50
  open, 46-64
  pole-effect, 50
  Pfund, 49
  rotating, 59
  silver, 58, 150, 231
  spectrographic, 49
  Sperry, 618
  starting, 46
  thallium, 48
  theory of, 46-48
  tungsten, 47, 50, 160
  underwater, 152
  zinc, 62, 231
Areca, tincture, 658
Arginine, 672, 677, 767
Argon, 132, 136, 138, 139, 141, 143, 147, 279, 466, 583
  effects on photoreactions, 296, 321, 327, 329, 331, 332, 460, 463
  excitation, 26
  in starting mercury arc, 77
  ionization potentials, 27
  lines in S-1 sunlamp, 144
Argyria, 744
Arnica, 657
Aromatic carboxylic acids, chlorination, 547
  compounds, halogenation, 542-549
  compounds, stability, 466
Arsenic, 333, 354, 358, 387
  acid, 369
  chlorides, 545, 549, 854
  sulfide sols, 389-391
Arsenicals, 549
Arsenites, 390, 750
Arsenous acid, 390, 750
  oxide, 167, 171
Arsine, 332, 333, 359, 387
  tetrachloro, 549
Artificial leather, 650
  rubber, 558
  silk, 613, 620, 621
  teeth, in black light, 178
Artura scale, 583
Aryl amines, 495
  azides, 648
  benzimidazoles, 743
  benzothiazoles, 743
  pyrrolinoanthranolazyls, 522
Arylideneacetones, semicarbazones, 491
Arythmias, heart, 862
Asbestine, 583
Ascaridol, 659
Ascaris eggs, 718
Asclepias, 890
Ascorbic acid, 710, 848, 849, 852, 867
Asparagine, 436, 672, 682
Aspartic acid, 671, 672
Aspergillus, 790, 887
Asphalts, 610, 661
Assimilation (see Carbohydrate photosynthesis)
Asthmas, 776, 824
Asymmetric photosynthesis, 266, 267, 404
Atmosphere, absorption by, 7, 191-202
  water photolysis in, 299
Atomic number, 21
  separation, 229, 232, 234, 235
  spectra, 19-22, 25, 230
  spectra, Bohr theory, 32, 33
Atom-molecules, 237
Atoms, excited, 26, 27, 229, 236-238, 257
  identification, 231
  in chain reactions, 252-254
  recombination of, 213, 231, 288
Atoxyl, 726
Atropine, 726, 760, 761
Aqueous humor, 762, 764
Aucubus leaves, 715
Auger effect, 241, 242
Auramine, 187, 643
Aurantia, 634
"Autoxypolymerization," 565
Avena seedlings, 888
Azelaic acid, 559
Azides, aryl, 481
Azidopropiondimethylamide, 266
Azidosalicylic acid, 481
Azine dye, 497, 640
Azobenzene, 336, 500, 603
Azobenzene dicarboxylic acid, 498
  hydroxy, 499, 562
Azo compounds, 499, 500
  dyes, 624-626, 630, 640, 643, 659
Azoisopropane, 459
Azomethane, 459, 460
Azonaphthalene, 503
Azonaphthol, 503
Azorubin, 638
Azoxyanisole, 499
Azoxybenzene and derivatives, 469-471, 496, 499
Azoxynaphthalene, 493, 503
Azoxyphenetole, 499
Azoxytoluenes, 499

B. *coli* (see *Escherichia coli*)
B. diphtheriae, 704
B. enteriditis, 825
B. leptisepticum, 776
B. mucosus capsulatus, 696
B. mycoides, 709
B. paratyphosus, 696
B. pasteurianum, 630
B. prodigiosus, 693
B. subtilis, 695, 696
B. typhosus, 693, 694, 696, 698
Bacteria, and irradiated oils, 727, 728
  and methylene blue test for milk, 762
  and nitrogen fixation in soils, 350
  antigenic properties, 706
  differentiation 706
  extracts, as sensitizers, 861
  growth, 886
  in air, 729
  in milk, 721
  lethal irradiation, 247, 692-707, 860
  luminous, 876
  pigment formation by, 888
  purple, 881
  sublethal irradiations, 696, 697, 828
  sulfur, 518
Bacteriolysins, 758
Bacteriophages, 711, 712, 860
Baicalinase, 684

Bakelite, 183, 584, 612
Baking, effect on vitamin D, 830
  industry, ultraviolet rays in, 722
Balata, 594, 602, 603
Ballast, for lamps, 141, 146
Ballistite, 462
Balloon fabric, 189, 608-611
Balmer series, 20, 22, 32, 52, 156, 163
Bamberger reaction, 470
Banana meal, irradiated, 829
  skin, pigmentation, 891
Bands, physical isolation, 189, 190
  Schumann-Runge, 293-295
  spectra, 52-63, 217-228
"Barium acid stearate," 265
Barium carbonate, 176
  fumarate, 454
  glass, 165
  ion, 377
  lines, 26
  maleate, 454
  metaphosphate, 172
  oxide, 50, 168, 169, 171
  platinocyanide, 261
  stearate, 265
  sulfate, 384, 582, 583, 605, 609, 869
Barley, germination, 885
Barrels, sterilization, 725
"Baryaire" equipment, 730, 731
Barytes, 359, 582, 583
Basal metabolism, 744, 746
Basic carbonate white lead, 582, 583
Basic colors, fading, 635
Batiste, 189
Bauxite, 359
Bean roots, 887
Beef, tenderizing, 724
Beer, 207
Beer's law, 207, 352, 365
Beeswax, 559, 743
Begonia, red pigment, 715
Belladonna, tincture, 658
Benedict's solution, 870
Benzal chloride, 526, 544, 545
Benzaldehyde, 451, 472-474, 496, 511
  and indium oxide, 360
  and nitrobenzene, 470, 471
  and potassium cyanide, 480
  and pyruvic acid, 451
  and rubber gelation, 595
  condensation product with acetophenone, 490
  derivatives, 472-476, 494, 498
  formation, 467, 470, 477, 478, 481, 483, 518, 526
  in sulfite oxidation, 356
  oxidation, 255, 423, 473, 474
  phenylhydrazone, 474
  photolysis, 468, 473, 474
Benzaldoximes, derivatives, 493, 494
Banzalephedrine, 688
Benzalpyruvic acid, methyl ester, 490-492
Benzamide, 340, 438
Benzanilide, 438, 470
Benzanthracene, 505
Benzanthrone, 595
  dihydro, 505
Benzaurin, 627
Benzene, 187, 244, 340, 407, 411, 451, 469, 478, 479
  absorption bands, 154, 155, 466, 467
  and nitrogen peroxide, 469
  and oxygen, 466
  behavior in electrodeless discharge, 36
  detection, 467, 651
  emulsions, 391
  filter, 189, 799, 829
  fluorescence, 466
  formation, 414, 458, 472
  halogenation, 527, 542-544
  homologs, 467
  nitration, 469, 470
  reaction with bromine atoms, 544
  ring, 183
  stability, 397, 466
Benzene derivatives:
  acetylchloroamino, 496, 497
  azocresol, 496
Benzene derivatives (*Continued*)
  azonaphthylamine, 603
  azophenylnaphthylamine, 626
  azoxy, 469-471, 496, 499
  diazonium chloride, 500
  diazonium compounds, 625
  dihydrohexabromo, 543
  dinitro, 469, 471
  diphenyl, 592
  diphenylamino, 562
  ethyl, 488, 546
  halogen substituted derivatives, 469, 474, 542-544, 546, 547
  hexahydroethyl, 473
  hydroperoxide, 468
  hydroxyazo, 496, 499
Benzidine, 260, 339, 479, 497, 498, 573, 610, 646, 672
Benzil, 478
Benzil dioxime, 498
Benzilic acid, 478
Benzimidazole, 852
Benzine emulsions, 391
Benzo colors, 638
Benzoflavine, 264
Benzohydrol, 476
Benzoic acid, 187, 344, 515, 640
  chlorination, 547
  esterification, 480
  formation, 467-470, 473, 474, 478, 481, 483, 484, 496, 506, 508, 514, 526
  photolysis, 480
  reaction with aniline, 438
Benzoic acids, amino, 498
  chloro, 477, 500, 546, 547, 549
  diiodobenzoyl, 498
  hydroxy, 480, 500, 546
  nitroso, 472, 474, 475, 516
  trinitro, 472
Benzoin, 478, 480
Benzonitrile, 494
Benzophenone, 340, 404, 430, 476-478, 480, 507
  alkyl oximes, 478
  carboxylic acid, 478
  diamino, 562
  dihydroxy, 474
  di(hydroxymethyl), 478
  dimethoxy, 477
  dimethyl, 477, 506, 547
  dimethylchloro, 478, 547
Benzopinacol, 430, 476-478
Benzopurpurin, 633
Benzopyrene, 511, 765, 865
Benzoquinone, 469, 474, 480
  absorption spectrum, 479
  and alcohols, 404, 480
  in photoöxidations, 507
  oximes, 471
  photolysis, 101
Benzothiazole, 183
Benzotrichloride, 526, 544, 545
Benzoylacetal peroxide, 473
Benzoxazole, 183
Benzoylacrylic acid, 491
Benzoylaminophenol, 496
Benzoylaniline, 496
Benzoylcamphor, 515
Benzoyl chloride, 401, 547-549, 834
Benzoylchlorophenylethylene oxide, 493
Benzoylethylene derivatives, 489, 493
Benzoyl peroxides, 410, 411, 415, 612, 834
Benzoylphenylhydroxylamine, 496
Benzoylpyridine, 520, 521
Benzylacetone, semicarbazone, 494
Benzylacetophenone semicarbazone, 494
Benzyl alcohols, 357, 471, 472, 526
Benzylamine, 495
Benzylaminobenzoic acid, 743
Benzyl benzoate, 592
  bromide, 545
Benzylcellulose, 463, 592
Benzyl chloride, 401, 496, 526, 544, 545
Benzylidene derivatives, 401, 472, 490, 493, 516-518, 522
Benzyl iodide, 399
Benzylmethylglyoxal, 451

Benzylphenylacetate, 478
Benzyl stearate, 589
Benzylpyridine, 520, 521, 646
Bergamot oil, and sunburn, 743
Berlin blue hydrosols, 390
Beryllia, 171
Beryllium carbonate, 172
  fluoride glasses, 170, 171
  phosphates, 172
Betaines, 626, 671
Biacetyl, 422, 427, 429-431, 440
Bidiphenylene-ethylene, antioxidant, 603
Bile acids, 669, 792
  as sensitizer, 861
Bilirubin, 745
Bios, 175
Biphenylenethylene, polymerization, 490
Birge-Sponer extrapolation, 235, 236
Bismarck Brown, 639
Bismuth, 150
  halides, 240, 411, 545
  in carbon arc, 58
  lamp, 148
  oxide, 508
  subgallate, 479
  triphenyl, 592
Bisulfite ion, 355, 357
Bitumen, 661, 662
Bivinyl, 408, 411
Black body radiation, 15, 16, 155
  light, filters for, 178, 179
Blackman reaction, 875-877, 879-881
Bleaching, of oils, 557
  solutions, 346
Blood, bactericidal power, 757, 775, 776
  calcium, 754, 755, 774, 776, 778, 783-785, 788, 818, 822, 823
  catalase, 685, 825
  cholesterol, 755, 773
  clotting, 746, 825, 862
  enzymes, 742, 756
  glutathione, 825
  irradiation, effects of, 703, 746-759
  lipids, 825
  phosphorus, 754, 774, 778, 779, 783-785, 788, 818, 822
  pressure, 733, 746
  purines, 703
  serum, 683, 746, 862 (see also Serum)
  sugar, 734, 751-753, 774
Blood (see also Erythrocytes and Leucocytes)
Bohr theory, 17, 21-25, 32, 33
Bond strengths, 217, 234
Bonds, conjugated double, 406
Bone ash, 786, 789
  calcification, 818, 822
  cultures, 818
  decalcification, 819
Bonnemasonia asperagoides, 713
Borax, 166, 171, 640
Boric acid, 172, 648
Borneol, 514
Bornyl chloride, 550
Boron, 64, 142
  halides, 64, 411
  hydrides, 359
  nitride, 139
  oxide, 75, 168, 169, 171, 176, 179
Botrytis cinerea spores, 696
Bottles, and stability of contents, 343, 346
Brackett series, 20
Bread, irradiation, 723, 830
Bredig sols, 388
"Brephos," 175
Breweries, use of ultraviolet rays in, 720
Brilliant Copper Blue, 633
  Green, 259, 264, 498, 627
  Safranine, 634
Broadcloth, 616
Bromaniline, isodiazotate, 646
Bromates, 348, 617
Bromic acid, 455
Bromides, 341
Bromine, 211, 214, 256, 345, 359, 540-546, 548-550, 760
Bromine, absorption spectrum, 181, 237, 249, 275, 345
  and carbon monoxide, 316
  and cinnamic aldehyde, 487
  and *cis-trans* conversions, 454-456
  and coumarin, 488
  and eleostearic acid, 565
  and diiodoethylene, 536
  and phenyl cinnamonitrile, 485
  and sulfur dioxide, 332
  as sensitizer, 307, 341, 485, 491, 535, 536
  atoms, 279, 280, 454, 455, 486, 537, 541, 544, 545
  Budde effect, 283
  excitation potential, 239, 373
  induced predissociation, 243
Bromodimethoxybenzoylacrylic acid, methyl ester, 491
Bromoethylbenzene, 546
Bromoethylbromomalonate, 542
Bromohydrocinnamic acid, 548
Bromomethoxybutyric acids, 541
Bromomethoxycinnamic acid, 487
Bromomethoxyhydroxybenzaldoxime, 494
Bromomethyl methylbenzoylbromides, 547
Bromonaphthoquinone, 502
Bromopentanes, 413
Bromophosgene, 316, 317, 346, 401
Bromosalicylaldehyde, 481
Bromosuccinic acid, 452
Bromotrichloromethane, 532, 533
Bromovinylacetylene, 415
Bronner's acid, 382
Brownian movement, 675
Brown-Pierce sarcoma, 766
Brucella abortus, 706
Bruchus obtectus larvae, 718
Brush discharge, 284
Buckwheat, 745, 861
Budde effect, 273, 282, 283
Bunsen-Roscoe law, 205, 474, 697, 698, 714, 767
Burdick air-cooled lamp, 728
Burns, treatment, 770
Butadiene, 408, 411, 596
  dicarboxylic acid derivatives, 493
  dimethyl, 502, 594
Butane, 258, 393, 394, 396, 429, 526, 531
  diiodo, 537
  diols, 833
  iso, 526, 531
Butene, 514, 536
Butoxybutadiene, 408
Butter, 556, 559, 560, 562, 563, 721, 817, 831, 835, 836, 854, 855
Butyl alcohols, 402, 403, 538
  bromide, tertiary, 399, 464
  butadiene sulfone, 413
  chloride, 531, 657
  iodide, 396, 397
  magnesium chloride, 464
  oleate, 589
  oxide, 657
  radicals, 429
  tartrate, 657
Butylene, 396
Butyraldehyde, 403, 421, 422
Butyric acid, 441, 477, 478, 540, 541, 710, 711, 727
  dihydroxy, 407
Butyroin, 451
Butyronitrile, 791

Cabbage, 689, 789, 830, 889
Cabomba caroliniana, 881
Cacao bean sterols, 831
  butter, 556, 817
  oil, 556
Cade oil, 513
Cadmium, and lithopone blackening, 385
  arc, 147-150, 231, 693
  as photosensitizer, 258
  halides, 240
  heat of dissociation, 234
  lines, 5, 150

Cadmium, oxide, 630
  photoelectric cell, 97, 99
  sols, 386, 387
  spark, 167, 259, 390
Caesium, 131, 238, 349
  iodide, 238, 342, 372, 373
Caffeine, 370, 522, 676
Calanus finmarchius respiration, 767
Calciferol, 806-809, 820, 821, 831
Calcification, 778, 779, 784, 785, 818, 822
Calcium, absorption, 745, 784-786, 818
  and muscle, 760
  dietary, 786, 820, 822, 824
  excretion, 818
  in blood, 754, 774, 776, 778, 779, 783-785, 788, 818, 822
  in carbon arc, 57
  in irradiated protozoa, 716
  in plants, 888, 889
  ions, 674, 682, 761
  lines, 26
  of skin, 742
  retention coefficient, 784, 786, 830
  salts, 763, 776
Calcium carbonate, 176, 583, 831, 869
  chloride, 184, 532, 704, 755, 763
  fluoride, 52, 57, 141, 168, 172, 349
  fructose monophosphate, 683
  glycerophosphate, 683
  hydroxide, 410
  lactate, 448, 540
  molybdate, 142
  oxide, cathodes, 131-133, 135, 136, 138
  oxyfluoride, 208, 349
  phosphates, 172, 359
  soaps, 586
  stearate, 410
  sucrose phosphate, 683
  sulfate, 582, 640
  tungstate, 142
Calibration, of photocells, 99
  of thermopiles, 96
  of ultraviolet meters, 100
Calico, 499, 616, 617, 633
"Callophane," 664
Calomel, 366, 367, 371, 444, 562
Calves, rickets, 786
Camomile, 657
Camphane, 550
Campholic acid, 515
Camphor derivatives, 268, 515, 516
Canaries, oxygen consumption by, 744
Cancers, 511, 766
Candlenut oil, 574
Cane sugar, inversion, 249, 390
Caouprene bromide, 409, 410
Caoutchouc, 608
Capelin, 790
Capillaries, dilatation, 748
Capri Blue, 264, 498
Caproic acid, 395
Capsicum, tincture, 658
Carbalkoxyarylindones, 453
Carbamide (see Urea)
Carbazole, 382, 504
Carbocyanines, 381
Carbohydrates, 431-436, 559, 695, 751-753
  absorption spectra, 670
  and nitrate reduction, 354
  photosynthesis, 259, 368, 866-882
Carbon, active, 508
  arc, actinometry, 104
    barium oxide in, 50
    biological effects of, 693, 733, 747, 748, 783, 784, 889
    carbides, in, 58
    cerium-cored, 54, 55
    disinfection by, 692
    Eveready, 60-62, 576
    flaming, 54, 527-529, 534, 578, 579, 581
    igniting gas mixtures, 291
    in therapy, 55-58, 62, 63, 771, 779, 836
    industrial, uses, 59, 60, 64, 579-581, 607, 618, 640-643, 645, 653, 723, 829, 832
    milk irradiating equipment, 842, 843
Carbon, arc, operation, theory of, 46, 47, 50, 51, 53, 59
    spectral energy distribution, 51, 53-56, 58, 61, 157
    underwater operation, 64
    with electrolyte, 59
    with filters, 61
    with hydrocarbons, 60
Carbon black, 600, 609, 610
  electrodes, 150
  in discharge tube, 141
  ionization potentials, 27
  isotopes, 227
  spark, 154
  spectral lines, 7, 42
Carbon dioxide, 144, 279, 343, 345, 393, 416, 539, 540, 883 (see also Carbohydrate photosynthesis)
  absorption by, 194, 307
  and dyes, 633
  and linen, 615
  and pheophorbide, 879
  and rubber, 601
  and smokeless powder, 462
  conversion to formaldehyde, 194, 868, 869
  dissociation, 240, 307
  effects on various photoreactions, 273, 296, 298, 308, 316, 327, 329, 361, 364, 428, 469
  formation, 64, 304, 310, 350, 394, 400, 403, 422, 425, 431-433, 437-442, 445, 447-452, 454, 456, 457, 461, 462, 469, 470, 477, 478, 480, 511, 514, 515, 518, 521, 614, 615, 626, 673, 674, 739, 863
  in accelerated tests, 580, 590
  in fermentation, 709
  in gasoline testing, 653, 654
  in milk sterilization, 722
  nascent, 870
  photolysis, 45, 307, 308
  photoreaction with hydrogen, 308
  reduction, mercury-sensitized, 258
Carbon disulfide, 62, 64, 354, 391, 463, 510, 833
  monosulfide, 354
  monoxide, 370, 393, 652
    absent near carbon arc, 51
    absorption spectrum, 308, 687
    adsorption on quartz, 309
    and dyes, 633
    and fermentation, 710, 711
    and fluorine, 317
    and peroxidase, 686
    and plant photosynthesis, 876
    -catalase compound, 685
    conversion to formaldehyde, 72
    effects on various photolyses, 296, 316, 322
    -ferrocystein compound, 687
    -ferroglutathione compound, 687
    filter, 309
    formation, 64, 307, 333, 334, 394, 395, 399, 402, 405, 416-418, 420-422, 424-434, 448, 449, 460-462, 465, 472, 473, 478, 521, 614, 671
    heat of dissociation, 235, 308
    -hemin compound, 687
    -hemoglobin, 687, 688, 749
    -indophenoloxidase compound, 686
    in mercury-sensitized water formation, 310
    in oxidation of nitrogen, 324
    in silent discharge, 310
    ion, 237
    iron-porphyrin compounds, 687
    oxidation, 250, 304, 308-313, 315
    photolysis, 308
    poisoning, 749
    reaction with amines, 322
    reaction with ammonia, 322, 458
    reaction with bromine, 316
    reaction with chlorine, 310-314
    reaction with ClO radicals, 312
    reaction with hydrogen, 310
    reaction with methanol, 439
    reaction with nitric oxide, 310
    -Warburg enzyme compound, 687
  Carbon suboxide, 308, 447
  Carbon subsulfide, 62, 64

Carbon tetrabromide, 345, 395, 401
Carbon tetrachloride, 182, 279, 359, 409, 526-528
  absorption spectrum, 395, 396
  and bromine oxide, 346
  formation, 532, 533
  in rubber cements, 597
  photoreactions of, 354, 400, 529
Carbons, arc, 51, 64
Carbonyl chloride, 539 (see Phosgene)
Carbonyl group, 416, 425, 426, 437
Carbonyl hypohalides, 440
Carbostyril, tetramethoxyphenyl, 484
Carboxy-acids, 467, 547
Carboxyl radical, 540
Carcinogenic agents, 765, 865
Carcinomas, 755, 766
Carmine II, 634
Carnauba wax, 410, 608
Carotene, 512, 555, 856, 871-873, 876, 882
  absorption spectrum, 853, 854
  and burns, 740
  and fermentation, 710
  and visual purple, 858
  as sensitizer, 862
  bleaching, 854, 856, 871
  conversion into vitamin A, 854
  formation, 888
Carrots, destruction of vitamin A, 856
Carvacrol, 513
Carvone, 515
Caryophylline nitrosite, 515
Casein, 583, 620, 674, 678
Cassia oil, 513
Castor oil, 411, 557, 559, 562, 574, 591, 612, 683
Catalase, 560, 680, 685, 742, 756, 825, 874, 877, 889, 890
Catalysts, 253, 254, 444, 498, 531, 532, 539
Cataplasms, 657
Cataracts, 763
Catechin, 479
Catechol tannin, 651
Catechu, 613
Cathode rays, 35, 152, 156, 657, 804, 828, 832
Cathodes, nickel, 160, 161
  nickel oxide, 132
  oxide-coated, 131-133, 135, 136, 138-140, 146, 151, 152, 160
  Schüler, 151
  sputtering, 139
  tungsten, 131, 161
  Wehnelt, 76, 131, 133, 156
Cattle, irradiation, 835
Celanese, 188, 643
Cell, absorption, 270, 271
Celloidin, 463
Cellophane, 185, 325
Cells, filter, 184
  photoelectric, 97, 99, 100, 107
  photronic, 96, 97
Celluloid, 9, 167, 407, 462, 463, 592
Celluloid-like products, 411
Cellulose, 562, 617, 618, 626
  acetate, 173, 463, 585, 588, 591, 640
  acetate silk, 188, 616
  acetobutyrate, 411
  and dyes, 633
  and flavanthrene, 635
  benzyl, 463
  derivatives, 589, 621
  deterioration, 613-617
  ester, 173, 621, 648
  ethers, 648
  ethyl, 463, 591
  hydrate, 167, 562
  lacquer, 51, 588
  nitrate, 462, 585, 591, 618
  regenerated, 173, 562
  tricrotonate, 621
"Cel-O-Glass," 170, 174, 175, 782
Cephalin, 669
Cereals, irradiation, 722, 789, 827, 829, 830
Ceresin, 610, 661
Cerevisterol, 792
Cerium, 23, 54, 97, 98, 174, 592
  fluoride, 51
  hydroxide, 390, 432, 450
Cerium, nitrate, 166
  oxide, 165-167
  perchlorate, 370
  peroxide, 573
Chaetopterus eggs, 764
Chain reactions, 213-215, 249, 252-255, 259, 356, 357, 497
  bromination of acetylene, 537
  bromination of cinnamic acid, 486
  chlorinations, 532, 535, 542, 543
  hydrogen-chlorine combination, 283-285, 287-290
  hydrogen-oxygen combination, 301, 302
  hydrogen peroxide photolysis, 340
  iodine-sensitized ethylene iodide photolysis, 536
  ozone photolysis, 297, 298
  styrene polymerization, 489
Chalcone and derivatives, 490, 491
Chalking, of paints, 577, 578, 581, 583, 589
Chalks, 575, 582
Charcoal, 171, 226, 341, 392, 469
Chardonnet silk, 188
Charges, electric, removing from paper rolls, 662
Checking, of paints, 577-579, 590, 603, 606, 607
Cheese, 563
Chemoluminescence, 265, 464, 878
Cherry-laurel water, 456
Chicago, antirachitic radiations at, 170, 173
Chicken food, antirachitic, 834
Chickenpox, 775
Chicks, and hay extract, 790
  encephalomalacia factor, 856
  irradiation, 787, 788
  leg weakness, 175, 202, 787
  phosphatase, 819
  rickets, 143, 781, 782, 813, 817, 837
China clay, 583
Chinawood oil, 564-567
Chlamydomonas eugamentos, gametes, 767
Chloral hydrate, 416
Chloramine, 105, 721
Chlorantin colors, 644
Chlorates, 307, 346, 348, 349, 617
Chlorazol dyes, 616, 633, 638, 642
Chlorella, 713, 714, 874-877, 882, 883
Chloretone, 717
Chlorhexane, 530
Chloric acid, 298, 346, 548
Chloride excretion, 760
Chlorides, 341, 343, 346, 348, 384, 439, 751
Chlorinated olefines, as solvents, 534
Chlorinated rubber, 611, 612
Chlorination catalysts, 531, 532, 539
Chlorinations (see the compounds chlorinated)
Chlorine, 187, 211, 215, 256, 291, 359, 400, 527-529, 531, 542, 543, 546, 547, 549, 550, 721, 760
  absorption spectrum, 181, 235, 237, 244, 249, 281, 282, 291
  and copper, 359
  and hydrogen atoms, 540
  and natural gas, 526-528
  as sensitizer, 259, 297, 298, 302, 303, 310, 314, 318
  attempted activation of, 284
  atom, 302, 306, 529, 532-535, 540
    reactions of, 213, 283, 284, 306, 313-316, 348, 540
  bleaching, 617, 618
  carrier, 544
  dissociation, 237, 282, 283, 287, 291, 311, 312, 314
  excited molecules, 269, 287, 290, 291, 311
  filters, 181, 182, 314, 800
  formation, 305-307, 347, 348, 361, 400, 451, 506, 546
  in milk sterilization, 722
  istotopes, 227
  of skin, 742
  photoexpansion, 282, 284, 285
  reaction with COCl molecule, 312, 313, 315
  reaction with formaldehyde, 418
  reaction with sulfur chloride, 355
  reaction with sulfur dioxide, 331, 332
  triatomic, 284, 288, 302, 311, 313
  water, 205, 346, 614

Chlorine dioxide, 243, 285, 306, 307, 347, 348
  heptoxide, 348
  hexoxide, 298, 307, 348
  monoxide, 305-307, 347, 348
Chlorites, 346
Chloroaminopyridine, 520
Chloroanthraquinones, 506, 507, 617
Chloranthrone, 508
Chlorobenzene derivatives, 543, 544, 546, 547
Chlorobenzoic acids, 477, 500, 546
Chlorobenzophenone, 477
Chlorobromobenzene hexachloride, 544
Chlorobromoethylbenzene, 546
Chlorocineole, 550
Chlorocinnamic acid, 483
Chlorocumene, 550
Chlorocyclohexene, 543
Chlorodibenzoylethylene, 489
Chloroethyl ether, 546
Chloroform, 528
  absorption and photolysis, 396, 400
  action of x-rays on, 209
  and quinine, 523
  chlorination, 532, 533
  formation, 452
  oxidation, 314, 532
  photolysis, 529, 400
Chloroformic acid, 539
Chlorohydroxyanthraquinone, 507
Chloroiodoethylene, 412
Chloromethoxybenzaldoxime, 494
Chloromethoxybenzophenone, 477
Chloronaphthalene, 549, 592
Chloronaphthoquinone, 502
Chloronitrodiaminotriphenylmethane, 626
Chloronitrosocyclohexane, 461
Chloronitrosophenol, 479
Chloroölefines, 531
Chlorophyll, 260, 261, 263, 264, 555, 791, 871, 888
  absorption bands, 870, 871
  and hydrogen, 679, 680
  absence of photoelectric effect, 872
  bleaching, 871, 872
  -carbon dioxide compound, 871, 875-877, 880
  chemoluminescent glow, 864
  diradical, 510
  fluorescence, 864, 877, 878
  formation, 886-888, 890
  green, 611
  orientation in chloroplast, 881
  peroxide, 863, 872
  photoactivity, 872
  photolysis, 680, 871
  photooxidation, 863, 871, 872, 878
  relation to carbohydrate photosynthesis, 862, 866, 872, 873, 877
  sensitizer, 434, 451, 490, 498, 522, 553, 560, 625, 626, 678, 749, 860, 862, 864
  skin sensitization by, 741
  -water complex, 877
Chlorophyllase, 873
Chlorophyllin, 872
4-Chloropicolinic acid, 520
Chloropicrin, 460
Chloroplasts, 715, 866, 871, 881
Chloroprene, polymerization, 596
Chloropropanes, 526, 531
1-Chlorosuccinic acid, 452
Chlorotoluenes, 544, 549
1-Chlorovinylacetylene, polymerization, 415
"Chlorozone," 288
Chocolate, irradiated, 831
Choke, for starting mercury arc, 92
β-Choladienic acid, 817
Cholanic acid, 817
α-Cholatrienic acid, 817
Cholehematin, as photosensitizer, 861
Cholera phage, 712
  vibrio, 706, 758
Cholestadiene, 817
Cholestantriol, 792
Cholesterol, 660, 756, 793, 812, 818
  absorption spectrum, 794
  antirachitic activation, 791-793, 795, 796, 802-804
Cholesterol, contaminants as provitamins, 813-816, 834
  7-dehydro, 794, 811, 815-817, 834
  dielectric constant, 794
  dihydro, 791, 794
  esters, 792
  fluorescence, 735
  in blood, 755, 773, 825
  in skin lesions, 742, 766
  irradiated, skin absorption, 847
  of wool, 623
  oxidation, 559
  sols, 669
Cholesterolized antigen, 758
Cholesteryl oxides, 792
Cholic acid, 670
Choline, 669, 677
Christiansen filters, 189
Chromates, 364
Chrome Green, 615, 633
  pigments, 582
Chromic acid, 206, 209, 251, 252, 364, 450, 524, 525
  hydroxide, 389, 404, 469
  sulfate, 439
Chromium, 167-169
  cations, 337
  chromate, 404
  coatings for arc carbons, 51
  complex salts, 363, 369
  hydroxide, 615, 633
  in cored carbon arc, 57
  lines, 26
  mirror in discharge lamp, 139, 142
  reflectors, 147
  salts, 187, 359, 443, 617
  trioxide green, 612
Chromophore theories, 624
Chromoprotein, in algae, 881
Chromosomes, 703, 704, 718
Chromotrope-2R, 260
Chromyl chloride, 365
Chrysiasis, 744
Chrysogen, 504, 511
Chrysoidine, 616
Ciba Blue, 616
Cibanone colors, 161, 616, 633
Cinchonidine, 524, 658
Cinchonine, 524, 525
Cinchoninic acid, 508
Cineole, 550
Cinnabar, 367
Cinnamaldehyde, 423, 474, 482, 484, 487
  nitro, 475
  semicarbazone, 494
Cinnamalmalonic acid, dimers, 485
Cinnamanilide, 484
Cinnamic acids, 185, 482-487, 490, 491
  and nitrobenzene, 470, 471
  formation, 474, 482
  halogenation, 255, 267, 485-487, 547
Cinnamic anhydride, 484
Cinnamide, 484
Cinnamon oil, 513
Cinnamonitrile, α-phenyl, 743
Cinnamylideneacetic acid, 484, 485
Cinnamylideneacetophenone, 485
Cinnamylidene-*m*-nitroacetophenone, 485
Circuits, electrical, for spark production, 39-42
  for starting mercury arc, 76, 77
  for underwater spark, 154
Circulatory system, and irradiation, 733, 746
Cis and *trans* compounds, absorption spectra, 412, 413
  interconversions, 457
Citraconic acid, 456
Citraconic anhydride, 806, 807, 834
Citral, 513
Citric acid, 369, 377, 648
  and ferric iron, 361, 362
  and pyridine, 518
  bromination, 540
  in tobacco, 884
  oxidation, 364, 448, 450
  reduction of stannic acid, 366

Citric acid, ultraviolet sensitizer for plates, 381
  uranium-sensitized photolysis, 450
Clark lithopone units, 716
Clay, in rubber, 610
Cleveland, solar energy at, 196
Cloth, 188, 189, 727
Clouds, effect on solar radiations, 198, 201
Clove oil, 513
Cluster theory, Weigert, 285
Coagulation time, blood, 746
Coal-tar, 512, 600, 865
Cobalt, 166, 167
  and lithopone blackening, 385
  cations, 337
  complex salts, 260, 368, 444, 445, 479
  drier, 572, 574, 592, 596
  glasses, 165, 168
  hydroxide, 368
  in carbon arc, 57
  lines, 26
  oxide, 165, 179
  salts, 187, 188, 359, 367-369, 403, 409, 444, 591, 596, 869, 870
  sulfate filter, 347
Cobra venom, 691
Cocaine, 268, 522, 658, 726
Cocoa, fluorescence, 556
Cocoanut oil, oxidation, 559
Codeine, 525, 726
Cod-liver oil, absorption spectrum, 555
  and calcium metabolism, 784, 785, 818
  and rickets, 779, 780, 786, 788, 813-815
  conductivity, 556
  irradiated, 728, 789, 791, 831
  oxidation, 559
Cod-liver oil, toxicity, 822
  vitamins, 780, 793, 820, 834, 838, 854, 855
Coenzymes, 680, 686-688
Coffee, 660
Coil, inductance, for starting mercury arc, 77
  induction, 136, 148, 149, 152
  preheating for starting mercury arc, 76
  Tesla, 153
Colds, and ultraviolet irradiations, 775, 776
Coleus, 886
Collagen, fluorescence, 651
Colletotrichum phomoides, 711
Collidine, 519
Collisions, deactivating, 215, 231, 335
  of first kind, 257
  of second kind, 257, 258, 261, 262
Collodion, 177, 462, 463, 479, 588, 627, 632
Colloidal systems, 64, 386-392
Collybia dryophila, 711
Color centers, in crystals, 373-375
Color photography, 627
Colpidium, sensitive molecules, 696
Coltsfoot, 657
Colza oil, 559, 612
Combustion, and ultraviolet rays, 652
Complement, 757-759
Complex radiations, summed effects, 255, 256, 441
Condensers, in production of sparks, 40-42, 153
Cones, of retina, 857
Congo Brown, 639
  Red, 389, 625, 633
  resin, 585
Coniferin, 436
Conjunctivitis, 164, 763
Conquinine sulfate, 521
Constant, Planck's, 8
  solar, 1
Cooper-Hewitt arc, (see Mercury arc)
Copal, 591, 610
Copper, 258, 359, 415, 442, 463, 546
  ammonia complex, 179, 188
  and chlorine, 359
  and ergosterol, 832
  and fatty acids, 554
  and methylene blue-alcohol dehydrogenase, 686
  arc, 47, 48
  compounds and benzylcellulose films, 592
  catalyst, 469
  cation, 337, 377
  cells, in actinometry, 105
  -egg white sensitizer, 553
Copper, in carbon arc, 57
  irradiated, 748
  line, 240
  number, 614, 616, 618-620, 633
  oxidation, 359
  salts, 184, 187, 188, 359, 362, 409, 498, 531, 553, 589, 603, 610, 617
  sensitizer, 265
  sols, 386, 389, 391
  underwater spark, 153, 155
Copper arsenate, in carbohydrate photosynthesis, 870
  carbonate, 522, 883
  hydride, 237
  hydroxide, 389, 657
  oxides, 179, 304, 442, 508, 563, 655
  soaps, 586
  sulfate, 184, 186, 187, 347, 357, 439
Coprosterol, 792
Corallin, 381, 629
Coramine, 520
Cordite, 462
Corex (see Glass)
Corium, of skin, 735, 736
Corn, 886-888
  meal, bleaching by sparks, 45
  oil, 557, 574
  silage, 790
Cornea, of eye, 164, 762
Corneum, of skin, 735, 736, 739
Corpuscular theory, 3
Corrosion, of metals, 661
Cosine law for intensity and angle of irradiated surface, 771
Cosmic rays, 9
Cotton, 188, 502, 608, 613-618, 620, 621, 626, 633, 637, 639, 646
  fluorescence, 645, 646
  printing, 495, 498
Cottonseed oil, 557, 558, 789, 847
Cotyledons, 886
Coumaric acids, conversion to coumarin, 488, 503
Coumarin, and derivatives, 487, 488, 503, 562, 609, 660
Coumarone-indene resins, 585
Counter, Geiger-Müller, 100
Cozymase, 686, 687
Crackers, irradiation, 830
Cracking of paints, 577, 578
  of rubber, 606, 609
Cragmor, solar energy at, 198-200
Crayons, 648
Cream, irradiation of, 841
Creatine, excretion, 745
Creatinine, 745, 858
Crêpe de Chine, 188
Crêpe rubber, 595, 598, 600, 602, 604, 605
Cresol, 390, 469, 479, 513
  dinitro, 499
  vinyl derivatives, 411
Cresolbenzene, 562
Cress seedlings, 715
Cresyl Blue, 365, 634
Cresyl Fast Violet, 634
Crocein, 629
Crocetin, derivatives, 767, 856
Crosin, 767
Crotalus terrificus toxin, 678, 691
Crotonaldehyde, 424, 425
Crotonic acid, 407, 455, 456, 541, 565
Crotonic amide, 455, 456
Crotyl cellulose, 591
Cruxite A, 166
Crystal Ponceau, 632
Crystal Scarlet, 625
Crystal Violet, 105, 627-629, 633, 634
Crystals, absorption spectra at low temperatures, 336
  anistotropic effects, 348, 353
  defects, and latent image, 374, 378
  diffraction of x-rays, 8
  lattice energy, 372, 378
  photoprocesses, 372-376
Cucumber plants, 885-888
Culture media, irradiation of, 709
Cumene, 550

Cumidine, 513
Cuminylidene hydrazones, 493
Cuprammonium rayon, 188, 613, 614, 621
Cuprene, 414
Cyanamide, 354
Cyanides, 265, 878
Cyanins, 183, 632, 634, 636
Cyanocyclopropane, and derivatives, 542
Cyanogen, 52, 53, 192, 218, 363, 456-458
Cyclobutane derivatives, 484, 492
Cycloheptanone, 429
Cyclohexane, 182, 407, 429, 466, 473
  carboxylic acid, 547
  1-chloro-1-nitroso, 461
  halogenation, 211, 542-544
  irradiation with air, 656
  nitration, 470
Cyclohexanol, 403
Cyclohexanone, and derivatives, 395, 403, 429, 516, 517
Cyclohexenes, 407, 413, 543, 547
Cyclohexenones, 516
Cyclohexylamine, derivatives, 612
Cyclopentane, and derivatives, 429, 448
Cyclopentanone, and derivatives, 429, 516
Cyclopropane, and derivatives, 395, 447, 466, 541, 542, 546, 653
Cyclops, 684, 767
Cylinder oil, 653
Cysteine, 433, 463, 673, 679, 750
Cystine, 623, 672, 673
Cytochrome, 687
Cytolysis, 716, 717
Cytosine, 677, 696, 699, 701

Dahlia, dye, 634
Dammar, 590, 610
Datura plants, 889
Davos, radiation at, 195
Decachlorocyclohexene, 543
Decalin, 511, 657
Decenic acid, 553
Dehydroascorbic acid, 848
Dehydrochlorophyll, 878, 879
7-Dehydrocholestene, 796
7-Dehydrocholestenopinacone, 817
7-Dehydrocholesterol, 794, 811, 813, 815-817, 834
Dehydroergosterol, 810, 812
Dehydrogenases, 686, 687, 760
Dehydrolumisterol, 810, 812
Dehydrorubrene, 603
7-Dehydrositosterol, 811, 816, 817
7-Dehydrostigmasterol, 817
Dental caries, 824
Dentistry, ultraviolet radiations in, 769
Dermatitis, 772, 861
Dermatol, 479
Dermatology, radiations in, 769, 861
Derris, 659
Desensitizers, 439, 440, 863
Designs, reproduction of, 648
Desoxycholic acid, 817
Deuteroflavin phosphate, 853
Deuterium, 290, 302, 320, 332, 394, 882
Deuterium iodide, 305, 344
Dewar flasks, filters, 187
Dextrins, 387, 388, 435, 436, 682
Dextrinosan, 435
Dextrose, 183, 339, 371, 383, 883
  absorption spectrum, 431
  and anthraquinones, 507
  and diastase, 681
  and methylene blue, 630
  fermentation, 709
  photolysis, 432, 433
  reduction of tungstic acid, 387
Diabetes, 752, 774
Diacetone alcohol, 427
Diacetoxyanthraquinone, 506
Diacetoxyhelianthrone, 506
Diacetoxynaphthadianthrone, 506
Diacetyl, 421
Diacetyl-diaminodiphenylamine, 497
Diacetylene, 415
Diagrams, energy-level, 27-29, 92, 219, 220, 229, 232-236
Dialdehydeazobenzene, 498
Dialkyl-diarylfumarates, 453
Diallyl, 594
Diallylthiocarbamide, 871
Diamagnetism, of crystals, 379
Diamin Fast Yellow, 616
Diaminoazoxytoluene, 499
Diaminobenzophenone, 562
Diaminonaphthalene, 497, 501
Diaminophenazine, 497
Dianisidine, 479
Dianthracene, 262, 504
Dianthraquinonylethane, 506
Dianthraquinone, dihydroxy, 506
Dianthrone, dimethoxy, 506
Diarylanthracenes, 508
Diarylmaleic acids, 454
Diastase, 680-682, 742, 752
Diatomic molecules, energy of, 232-234, 240
Diatoms, 790
Diazoaminobenzene, 575
Diazobenzenesulfonic acid, 500
Diazocamphor, 516
Diazo compounds, 460, 499, 500, 647, 648
  in actinometers, 105
  in textile printing, 645
  photolyses, 624, 625
Diazo, diphenylamine sulfate, 625
1-Diazo-2-hydroxy-3-naphthoic acid, 648
Diazomethane, 460
Diazonaphtholsulfonic acid, 624, 625
Diazonium salts and textile printing, 646
Diazo papers, 647, 648
Diazo printing, 645, 647
Diazo process, in photography, 384
Diazosalicylic acid, 481
Diazosulfanilic acid, 499, 500
Diazotized aniline, 646, 647
Diazotypes, 647, 648
Dibasic acids, 440-448
Dibenzalacetone, 743
Dibenzanthrene, 765
Dibenzofuran, 592
Dibenzoylbromoethylene, 489
Dibenzoylcyclobutane, 492
Dibenzoyldibromoethylene, 489
Dibenzoyldichloroethylene, 489
Dibenzoyldimethylnaphthalene, 549
Dibenzoyl peroxide, 480, 722, 723
Dibenzoyl-tetraphenyltetrahydropyran, 268
Dibenzyl ether, 405
Dibromobenzoylbenzoic acid, 498
Dibromoethane, 440
Dibromoethylene, 412, 537
Dibromoisatin, 616
Dibromomethoxyphenylpropionic acid, 487
Dibromopinacolone, 539
Dibromopropane, 546
Dibromophenylcyclopropane-1,2-dicarboxylic acid, 541
Dibromosalicylic acid, 548
Dibromotetrachlorethane, 401
Dibutyl phthalate, 481, 576, 612
Dibutyl tartrate, 173
Dichloracetic acid, 401
Dichloracetyl chloride, 401, 407
Dichloroacetylene, 538
Dichloroanthracene, 703
Dichloroanthraquinone, 506
Dichloroazoxybenzene, 499
Dichlorobenzene, 543
Dichlorobenzene, hexachloride, 543
Dichlorobenzoic acid, 549
1,5-Di(*o*-chlorobenzoyl)-naphthalene, 549
Dichlorocamphane, 550
Dichlorocineole, 550
Dichloroethane, 401, 526
Dichloroethylene, 412, 413, 535, 537
Dichlorodimethylbenzoylchloride, 548
4,4-Dichloro-1,3-dithiacyclobutane-2-one anil, 464
Dichlorohydrindones, 517
Dichloromethane, 526, 532
1,2-Dichloro-2-methylpropane, 532

1,2-Di(chloromethyl)2-methylpropane, 532
Dichloromethyl sulfate, 538
1,3-Dichloro-2-phenylpropane, 550
Dichloropyridine aldehydes, 520
Dichlorotoluene, 549
Dichroism, circular, 266, 383
Dichromates, 363-365, 384, 721
Dichromic acid, 524
Dicinnamalacetone, 485
Dicyclohexylamine, 612
Dicyclopentadiene, 538
1,5-Di(2,5-dichlorbenzoyl)-2,6-dichloronaphthalene, 549
2,4-Di(dichloromethyl) benzoyl chloride, 548
Didymium, 167
Didymium glass filter, 177, 178, 616
Dielectric constants, 249, 253
Diethyl-allylthiocarbamide, 631, 871
Diethylaniline, 643
Diethyl collidenedicarboxylate, 519
Diethyl cyclopropane-1,1-dicarboxylate, 447
Diethyl dibromosuccinate, 454, 455
Diethyl 2,6-dimethylpyridine-3,5-dicarboxylate, 520
Diethyl diphenylfumarate, 453
Diethyl diphenylmaleate, 453
Diethylene dioxide, 833
Diethyl ether (see Ether)
Diethyl ketone, 421, 428, 595
Diethyl maleate, 407
Diethyl phthalate, 173
Diethyl tartrate, 407
Diethyl toluhydroquinone benzoate, 474
Diffraction, 3, 4, 6-8
Difluorenylene, 511
Diffuse bands, 241, 243
Diffuse series, 23, 24
Diffusion, and temperature coefficients, 248
Di-furoyl peroxide, 517
Digitalis, 268, 658, 890
Digitonin, 670, 793
Diglycol, 405
Diglycollic acid, 405
Dihydrobenzanthrone, 505
Dihydrochalcone, 490
Dihydrocholesterol, 791, 794
22-Dihydroergosterol, 811-813, 817, 834
Dihydroisophthalic acid, 481
Dihydronaphthalenes, 501
Dihydronaphthylacetic acid, 511
Dihydrophytosterol, 791
Dihydrorotenone, 659
Dihydroxyacetone, 339, 404, 428, 432
Dihydroxyanthraquinone, 469
Dihydroxybenzaldehyde, 498
Dihydroxybenzophenone, 474
Dihydroxybutyric acid, 407
Dihydroxydianilinoindophenol, 497
Dihydroxydianthraquinone, 506
Dihydroxy-dinaphthyl-diquinone, 502
Dihydroxydiphenylpropane, 612
9-(2′,3′-Dihydroxy-1′-isopropyl)-isoalloxazine, 852
4,4-Di(hydroxymethyl)benzophenone, 478
Dihydroxyphenols, 833
Dihydroxyphenylalanine, 671
Diindyl-*m*-methoxy-*p*-hydroxybenzylidene, 517
Diiodobenzoylbenzoic acid, 498
Diiodobutane, 537
Diiodoethane, 400
Diiodoethylene, 399, 536
Diiodomethane, 400
Diisoxazole ketone, 517
Diisoxazolepinacol, 517
Diketones, 404, 429, 431, 478, 514
Diketopiperazines, 674
Diketostearic acid, 574
Dimethoxyanthracene photoöxide, 508
Dimethoxybenzaldoxime, 494
Dimethoxybenzbianthrone, 506
Dimethoxybenzophenone, 477
6,7-Dimethoxy-1-benzyl-*N*-methyl-1,2,3,4,tetrahydroquinoline-1-carboxylic acid, 521
Dimethoxydianthrone, 506
Dimethoxyhelianthrone, 507
Dimethoxynaphthadianthrone, 507
Dimethoxyphenazine, 497, 498
Dimethoxypyrene, 562
Di-*p*-methoxystyryl ketone, 489
Dimethylacetaldehyde, 421
Dimethylalloxazine, 852, 853
Dimethylaminoacetophenone, 629
Dimethylaminobenzaldehyde, 498
Dimethylamino-methylcoumarin, 609
Dimethylaniline, 497, 643
hydroxy, 497
Dimethylanthraquinone, 506
Dimethylbenzophenone, 477, 506, 547
Dimethylbenzoyl chloride, 547, 548
Dimethylbutadiene, 502, 594
Dimethyl carbonate, 539
Dimethylchlorobenzophenone, 547
Dimethylcoumaric acid, 503
Dimethylcoumarin, 503
Dimethylcyclohexenone, 516
Dimethylcyclohexyl adipate, 650
2,2′-Dimethyl-9,9′-dihydroxy-1,1′-dicarboxylic dilactone, 507
bis(Dimethylbenzoyl)ethylene, 489
Dimethyldiphenyltruxone, 517
Dimethyl ether, 405, 459
Dimethylethylene, 429
Dimethyl fumarate, 453
Dimethylhexene, 461
Dimethyl-*n*-hexyldimethyl carbinol, 428
Dimethyl maleate, 453
Dimethylphenazine, 497
2,3-Dimethyl-1,4,11,12-tetrahydrophenanthrenequinone-11,12-*endo*-2′3′-dimethyl-2′-butene, 502
Dimethylditolyl fumarate, 453
Dimethylditolyl maleate, 453
Dinaphthalene azotide, 497
Dinaphthazine, 497
Dinaphthylanthracenes, 508
Dinitroazoxybenzene, 499
Dinitrobenzaldehyde, 475
Dinitrobenzene, 469, 471
Dinitrobenzoyl chloride, 834
Di-*o*-nitrobenzylideneerythritol, 472
2,5′-Dinitro-5,5′-dimethoxydiphenyl disulfide, 500
Dinitronaphthalenesulfonic acid, 501
Dinitrophenol, 499
Dinitrotetrammine cobalt, 368
Dinitrotoluene, 470-472
Dinitrotriphenylmethane, 626
Dinitrosohydroxybenzyl alcohol, 471, 472
Dioxytriphenylnaphthacene, 511
Diparatungstic acid, 369
Dipeptides, 674
Dipentene-3-methane, 514
Diphenosuccindan-9,12-dione, 550
Diphenyl, 480
Diphenylacyldiphenylmethane, 493
Diphenylallyl ether, 493
Diphenylamine, 462, 591
Diphenylaminobenzene, 562
Diphenylanthracene, 508, 510
Diphenyl-4,4-*bis*-(8-azo-*N*-phenyl-*β*-naphthylamine), 626
Diphenylbenzene, 592
Diphenylbenzopinacol, 477
Diphenylcyclobutane-2,4-diatroponitrile, 484
Diphenacyldiphenylmethane, 521
Diphenylene ethylene, 408
Diphenylethane, 478
Diphenyldimethyltruxones, 492, 493, 517
Diphenyl-*bis*-diphenylenethane, 626
Diphenyl-di-2-pyridylethane, 520
Diphenylfurazan, 498
Diphenylglyoxime, 461
Diphenylguanidine, 592, 605, 610, 612
Diphenyl ketone, 595
Diphenylmethane dyes, 640
Diphenylnapththacene, 510
2,3-Diphenyl-*α*-*β*-naphth-1,2,3-triazolium picrate, 626
1,3-Diphenyl-2,4-*bis*-(*β*-phenyl-*β*-cyanovinyl) cyclobutane, 484
Diphenyltruxone, 493, 517
Diphosgene, 539
Diphtheria, 825
bacillus, 704

Diphtheria, toxin, 690, 691
Dipropylglycol, 403
Dipropyl ketone, 429
Diradical, rubrene, 509
Direct dyes, 616, 635, 642
Direct Scarlet, 390
Diricinoleic acid, 554
Disaccharides, 434
Discharge, electrical, classification, 30, 32
electrodeless, 36, 37, 157
glow (see Glow discharge)
hydrogen (see Hydrogen, discharge)
mercury (see Mercury, discharge lamps)
silent, 292, 310
Disilane, 333
Displacement law, Wien, 94
Dissociation, 212, 214, 216, 218, 227, 229-244
Distyryl ketone, 489
Disulfides, 463
Distemper, 777
Ditetrahydrofurfurylamine, 612
1,2,7,8-Di-(1,5-tetrazo)-4-methyl-(1,8-naphthyridine, 1,2,7,8-tetrahydride), 503
Dithiocyanoethanes, 457
Dithiocyanoethylene, 457
Dithionate ion, 355, 356
Di-*o*-tolylguanidine, 605
2,4-Di(trichloromethyl)benzoyl chloride, 548
Diuresis, 760
Divinylacetylene, 415
Dodecachlorocychlohexane, 543
Dodecylaldehyde, 424
Doebner's violet, 629
Döppler effect, 231
Dogfish oil, 853
Dogs, 745, 786
Dopa, formation, 671
Dough, irradiation, 723
Dragon's blood, 610
Draper effect, 284, 285
Drosera whittakeri, 502
Droserone, 502
Drosophila, 703, 765
Drugs, and light, 268, 657, 658
Dryco, irradiated, 827
Drying oil substitute, 584
"Dual purpose" sources, 142-147
Duco, nitrocellulose enamel, 586
Dulcitol, 1,2,5,6-di-*o*-nitrobenzylidene, 472
Duranthrene yellow, 633
Durophen lacquer, 592
Dust, 196, 201, 202, 340
Dyeing, aniline black, 495
nitronaphthalene derivatives, 501
Dyes, absorption, 624
and carbohydrate photosynthesis, 869, 873
and cotton tendering, 615, 617, 643
and gasoline, 657
and irradiated wool, 622
and perfused heart rhythm, 761
and potassium dichromate, 634
and rubber oxidation, 601, 603, 609, 610
and Weigert effect, 383
as photosensitizers, 259, 260, 263, 264, 381, 556, 712, 745, 832, 862
associated, 264
azine, 497
azo, 624, 630
Dyes, basic, 485
diphenylmethane, 640
direct, 390, 616, 635, 642
excited, 263, 264
fading, 103, 205, 206, 259, 384, 631-635, 863, 864
fluorescent, 260-264, 463, 600, 645
for airplane wings, 643
for balloon fabrics, 608
for filters, 177, 182, 632
halogenated, 507
in paper, 644
in textile printing, 645
nitrated, 633
peroxide formation, 863, 864
phthalein, 629
tests for light fastness, 443, 578, 634-642
Dyes, triphenylmethane, 626-629, 632
vat, 616, 617, 630, 642, 647
Dypnone, 490, 494
Dysentery phage, 712

Earthworm, porphyrin, 767
Eastman sensitizer, 382
Eastman UV spectroscopic plates, 160
Ebonite, 584, 608, 609, 611
Eclampsia, therapy, 774
Eczema, 769, 824
Eder reaction, 443-445
Edestin, oxidation, 678
Egg yolk, sterols, 789, 816
Eggs, 717, 718
antirachitic properties, 787, 827
Arbacia, 764
Chaetopterus, 764
hatchability, and production, 787, 788
sea urchin, 764
starfish, 764
Eigenfunctions, 26
Einstein equivalence law, 207, 210, 211, 213, 222 266, 342, 351, 355, 732, 802, 863, 874
unit, 207
Elaidic acid, 565
Elder blossoms, 657
Electrical discharges, classification, 30, 32
Electricity, static, removal from air, 662
Electrodes, (see also cathodes and mercury arc)
aluminum, 156, 157, 159
arrangement for sparks, 42-44
brass, underwater spark, 153, 155
carbon, 150
for discharge tubes, 133, 135, 140, 339, 364
for many-lined emission, 152
Electrolysis, intramolecular, 371
with irradiated cathodes, 339
Electromagnetic spectrum, 2, 3, 6, 9, 10
Electrometer, 97
Electron, accelerated, 8, 9
affinities, 263, 337, 338, 372, 378, 438
alloy, 661
bombardment, 209, 229, 348, 354
diffraction, 11
displacements in crystals, 373, 374
energy levels, 218, 220
high-velocity, lethal action of, 705
orbits, 26
primary, 31
secondary, 31
temperature in arc plasma, 48, 94
transitions, 22-24, 227, 337, 338
ultimate, 32
Electron-volt, 8, 220
Electrophoresis, 387, 388, 704, 751
Electroscope, gold leaf, 97
Elements, discovery, 662
in sun, 192
transitional, absorption spectra, 337
Eleomargaric acid, 564
Eleostearic acid, 564-566, 574
Elixir of pepsin, 658
Elodea canadensis, 715
Embryonation, roundworm ova, 718
Embryos, 718, 765
Emetine, 760
Emission, of radiant energy, quantum theory, 15-30
Emulsin, 680
Emulsions, 391, 657
gelatin, 266, 379, 380
of bacteria, 693, 694
Enamels, accelerated weathering tests, 586, 587
Enanthaldehyde, 423
Encephalitis virus, 712
Encephalomalacia factor, 856
Endocrine organs, 790
Energy, and mass equivalence, 191
intramolecular migration, 427
levels, 17, 21-23, 26-29, 92, 218-220, 222, 223, 226 230
Engine oil, irradiation of, 653
Entropy, 217

1,2 ...-688, 727, 853, 891
D... ...s, 874, 876, 880
... 247
... 703
... 339, 344, 381, 383, 390, 633
... 433, 444, 445, 451, 498, 553,
... 595, 678, 682-684, 688, 703, 725, 812,
..., 862, 863, 865
...ological stains, 631
... therapy, 772
lake, 642
photolysis, 498
Ephedrine, 688
Epichlorhydrin, 497
Epicholesterol, 792
Epidermal cells, *Aucubus* leaves, 715
Epidermis, 693, 735-737, 739, 772, 809
Epihydrinaldehyde, 553, 560
Epilepsy, 776
Equilibrium constants, 217
Ergometrine, 525
Ergopinacol, 812
Ergostatriene, 796
Ergosterol, absorption spectrum, 795-797
and corona discharge, 832
and fermentation, 709
and tobacco, 660
as provitamin, 794-803, 813, 814, 816
color reactions, 796
dehydro, 810, 812
22-dihydro, 811-813, 817, 834
in soaps, 847
in skin lesions, 742
irradiated, 782, 800-807, 809-811, 819, 828, 831, 832, 834
sensitized reactions, 812, 862
peroxide, 812
production, 832
separation from vitamin D, 833
structure, 795, 796, 809, 811
unimolecular films, 811
Ergosteryl acetate, 804, 812
Ergot, 525, 795, 796, 828
Ergotetraene, 812
"Ertron," 832
Erythema, 673, 733-742, 744, 754, 757, 759, 773, 775
induratum, 769
production and reciprocity law, 101
radiations causing, 103, 105, 197-199, 628
tests for dosage in therapy, 102, 771, 783
Erythritol, di-*o*-nitrobenzylidene, 472
Erythrocytes, 746-750, 758, 818, 860, 863, 865
Erythrosin, 264, 381, 390, 634
as sensitizer, 490, 554, 863
photolysis, 498, 629
Erythrulose, 432
Escherchia coli, 693, 694, 698, 704-707, 711, 712, 757, 775
Esculin, 390, 562, 629, 743
Eserine salicylate, 522, 726
Esparto, 644
Essential oils, 513-515, 727, 728
Ester gum, 585, 590, 591
Esters, absorption spectra, 437
as polymerization inhibitors, 410
chlorinated vinyl, 410
formation in plants, 882
hydrolysis, 436
in fermentation, 709
Ethane, 258, 406, 440
diphenyl and derivatives, 478, 520, 626
effect on acetone photolysis, 428
formation, 396-398, 406, 407, 414, 418, 425-427, 429, 431, 448, 458-460, 464
halogenated, 400, 526, 528, 533-535, 537, 613
photolysis, 393, 394
Ethanol, 340, 365, 366, 369, 433, 449, 471, 514
absorption of light, 401, 402
addition to crotonic acid, 455
and chloroform chlorination, 533
as polymerization inhibitor, 410
bromination, 538
Ethanol, formation, 397
oxidation, 403, 404
photolysis, 402
reaction with ketones, 403, 514, 517
Ether, chloroethyl, 546
diethyl, 540
dimethyl, 405, 459
diphenylallyl, 493
Ethers, 361, 405, 467, 510
Ethoxyanilines, 498
Ethoxybenzoylacrylic esters, 491
Ethyl acetate, 340, 356, 431, 436
acetoacetate, 431, 630
alcohol (see Ethanol)
Ethylamine, 322, 340, 403, 408, 458
Ethylanthracene, 509
Ethylbenzene, 488, 546
Ethyl benzoate, 340
benzoylacrylate, 491, 492
bromide, 396
bromocyclopropanedicarboxylate, 542
bromopropionate, 266
Ethylcarbazole, 382
Ethylcellulose, 463, 591
Ethylchlorophyllide, 862, 863, 872
Ethyl cinnamate, 340
cinnamylidenecyanoacetate, 484
Ethylcoumaric acid, 488
Ethyl cyanocyclopropanecarboxylate, 542
Ethylcyclopropane, dicarboxylate, 542
Ethyl diazoacetate, 460
dibromocyanobutyrate, 542
dihydrocollidine dicarboxylate, 382
diphenyl-lactate, 493
diphenylrubrenedicarboxylate, 510
ether, 540
fumarate, 454, 455
green, 634
iodide, 246, 336, 396, 397
ketopentadienedicarboxylate, 489
maleate, 454, 455
malonate, 540
mercaptan, 463, 465
Ethylmethylmaleimide, 872
Ethyl nitrite, 461
nitrobenzylidene malonate, 548, 549
oxalisobutyrate, 493
peroxide, 397
phenylacetate, 340
Ethylphenylanthracene, 508
Ethylphenylindone, 493
Ethyl radical, 396, 408
red, 381
Ethylthiolactic acid platinum, 464
Ethyl toluidineobutyrate, 456
Ethylene, 393, 406-408, 440, 833
and methylene radicals, 430
formation, 396, 398, 399, 414, 422, 429, 430, 458, 460, 514
halogenation, 534, 537
hydrogenation, 258
Ethylene, benzoyl derivatives, 489, 490, 493
biphenylene, 408, 490
dibromo, 537
dichloride, 534, 535, 537
diiodide, 399, 400, 536, 537
dimethyl, 429
glycol, 399, 404, 407, 408, 410, 562, 660
oxide, 493, 612
perchloro, 657
phenyl, 488
tetrachloro, 534, 535, 657, 659
trichloro, 529, 535, 657
trimethyl, 594
Etioglaucobilin, 680
Etioneoxanthomethenes, 680
Etioporphyrin, 680, 872
Eucalyptus oil, 513
Euchoris multicornis, 767
Eugenol, 513, 514
Euglena, lethal action on, 713, 888
"Eyeready" therapy units (see Carbon arc)
"Everfast" suitings, 616
Excited molecules, 214-216, 242, 251
states, 220, 226, 232, 243

Exciton, 375, 379
Exclusion principle, 25
Excreta, antirachitic action of, 780
Exploded wire, ultraviolet source, 35, 36
Explosions, 209
Explosives, smokeless, 462
Extinction coefficients, 249, 250, 271
Eye media, 762-764
Eyes, protection from radiations, 164

F acid, and photopyridine, 519
F color centers, 373, 374, 375
Fabrics, 188, 189, 613-617, 621, 635, 645
Fade-Ometer, 508, 578, 608, 616, 617, 622, 623, 633-635, 641-644
Falk electrophoresis cells, 704
Faraday dark space, 30, 31
Farina, irradiated, 830
Farmer's skin, 769
Fast Orange, 634, 639
Fast Scarlet, 5, 639
Fat, absorption spectrum, 670
and erythema, 741
and milk irradiation, 762, 844
beef, 559, 560
fluorescence, 556, 600
formation in plants, 882
irradiation, 789, 827, 831
metabolism, 826
oxidation, 559
sterilization, 721
Fatty acids, 508, 553, 554, 559, 652, 669
Fehling's solution, 614
von Fellenberg test, 561
Fenchone, 514
Fermentation, 432, 660, 709, 710, 826
Ferns, prothallia of, 714
Ferric acetyl acetone, 465, 595
chloride, 205, 410, 411, 469, 503, 531, 532, 539, 544, 553
and chlorophyll, 872
and gelatin, 384
and rubber, 595
as sensitizer, 441, 442, 867
catalyst, 883
crystal, light absorption, 360
photolysis, 360, 361
reduction by organic acids, 441, 443, 448, 450
gluconate, 451
hydroxide, and cotton, 614, 615
catalyst for photosynthesis, 868, 870
sol, 389-391
ion, 344, 360, 448, 451, 631
nitrate, 522
oxalate, 255, 445
oxide, 167-169, 171, 577, 870
resinate, 619
salts, 361, 362, 384, 444, 449-459
sulfate, 359, 362
Ferricyanide ion, 341, 362, 363
Ferrites, 173
Ferrocyanide, 341, 354, 362, 363, 630
Ferrocysteine-carbon monoxide compound, 687
Ferrous acetyl acetone, peroxide, 465
carbonate, 831
chloride, 361, 367, 553, 872
hydroxide, 360, 362, 450
iodide, oxidation, 254
ion, 263, 344, 360, 439, 455, 686, 881
oxide, 167, 168
resinates, 619
salts, 444, 449, 588, 589, 669, 702, 868
sulfate, 359, 360, 364, 443, 455, 631
action of X-rays on, 209
and chlorophyll, 871
oxidation by benzoquinone, 480
reaction with iodine, 344, 345
sulfide sol, 390
thiocyanate, 358
Fertilizers, 662
Fertilizin, 764
Fibrinogen, 676, 678, 825, 862
Films, photographic, transparency, 585
Filter, 177-189
ammonium thiocyanate, 347
and irradiation of marine organisms, 717, 718
benzene, 799, 829
caffeine, 370
carbon disulfide, 833
chlorine, 314, 800
cobaltous sulfate, 347
copper sulfate, 347
Corning G 586 AW, 889
for accelerated paint tests, 580
for actinometry, 102, 103
for irradiating ergosterol, 833
infrared, 126, 178, 186
in irradiating foods, 828, 829
in measuring energy distribution, 96-101
in studies of bacterial action, 692
lead acetate, 726
methylene blue, 744
nickel oxide, 663
paper, 619
photographic, 178, 632
postassium nitrate, 800
quinine sulfate, 347
Schott glass, 864
silver-leaf, 150, 178, 762
to remove rays shorter than 3200 A., 150
Wood's glass, 781
xylene, 829
Filtray A, 166
Fish, antirachitic potency, 827
oils, absorption bands, 853
Fish-livers, origin of vitamin D, 790
Flagella formation, 767
Flaking of paints, 577
Flames, 35, 663
Flaming arc (see Carbon arc, flaming)
Flannel, 188
Flavanthrene, and cellulose, 635
Flavin, 686, 850-853, 857-859
Flax, 613, 645
Flex-o-glass, 170
Flexometer, 587
Floridin, 794
Floridoside, 436
Flour, bleaching, 45, 722
Flowers, 178, 715
Fluoray, 664, 852
Fluorene, 382, 490, 504
amino, 511
phenyl, 512
Fluorenene, 476, 477, 511
Fluorescein, 260, 262, 339, 390, 864
as sensitizer, 725, 865
destruction, 629
sodium, 864
surface tension, 503
Fluorescence, 105, 150, 207, 213-215
and Eder reaction, 444, 445
and nature of spectra, 230, 231, 242, 243
and sensitization, 260-263, 862
and tetraphenylrubrene oxidation, 510
analysis, 178, 575, 663-665, 852
in tanneries, 651
of dyes, 645
of fats and oils, 556, 557, 559
of ink, 644
of lacquers, 591
of paper, 620
of resins, 158
of rubber accelerators, 600, 601
of textiles, 624
assay, flavins, 852
benzene, 466
catalase, 685
Chlorella, 877
chlorophyll, 864, 877, 878
efficiency, 261, 262
glass, 176
hydrogen peroxide, 304
in radiation measurement, 100
of skin, 734, 735
pheophorbide-b, 879
quenching, 231, 257, 260-264, 335
textiles, 624

Fluorescence, theory, 261, 665
ultraviolet, in biology, 733
yeast respiratory enzymes, 687
Fluorescent lamps, 142, 152
Fluorides, 171, 172, 657
Fluorine, 238, 274, 317
oxide, 349
Fluorite, 7, 151, 208, 349, 698
Fluoroheptachlorocyclohexane, 544
Fluorometers, 105
Fog nuclei, 387
Follicular hormones, 689
Fomes pini, 889
Foods, irradiation, 721-724, 788-791, 827-831
Foot-and-mouth disease, virus, 712
Forbidden lines, 24, 92
Formaldehyde, 173, 258, 308, 310, 315, 316, 368, 435, 439, 573, 612, 705, 883
absorption spectrum, 416
and ammonia, 522
and lethal action of radiations, 695
and nitrites, 882
and tryptophane oxidation, 671
condensation with urea, 584
conversion to alcohol, 418
dissociation, 240
formation, 72, 308, 396, 397, 399, 400, 402, 403, 428, 433, 434, 439, 441, 451, 462, 465, 525, 873
from egg albumin, 676
in atmosphere, 194, 869
in plant photosynthesis, 866-870, 877, 880
oxidation, 418, 422, 434
photolysis, 240, 416, 417, 420, 422, 425
polymerization, 416
production from water gas, 259
reaction wtih chlorine, 418
reduction of tungstic acid, 387
Formamide, 322, 458
Formhydroxamic acid, 882
Formic acid, 308, 369, 418, 469, 584, 695, 878, 883
absorption spectrum, 437
and chlorophyll bleaching, 872
chlorination, 539, 540
-formate buffer, 364
formation, 399, 404, 407, 422, 440, 460, 467, 468, 480
in plant photosynthesis, 867, 868, 880
oxidation, 440
photolysis, 246, 422, 437, 439, 440
Formose, 867
Formyl chloride, 418
Fractures, healing rate, 819
Franck-Condon principle, 236, 242
Franck-Haber theory, 355
Fraunhofer lines, 4, 6, 18
Free energy, 217
radicals, 231, 397, 421, 424-426
Frequency, 5
Friedlander's bacillus, 720
Frog eyes, oxygen uptake, 764
larvae, 765, 766
muscle, 678
Frost injury of plants, 887
Fructose, 432-434, 521, 710, 867, 883
nitrobenzylidene acetal, 472
Fruit, composition after irradiation, 891
juices, sterilization, 722, 725
Fuchsin, 179, 182, 264, 382, 498, 629
Fucoxanthin, 882
Fulgides, 493
Fumaric acid, 412, 451-455, 541, 764
Fumaronitrile, 457
Fundamental frequency, 233-235
series, 23, 24
Fungi, 711, 860, 886, 889, 890
Fungisterol, 796
Furandicarboxylic acid, 515
Furazan, diphenyl, 498
Furfural, stability, 466
resins, 584
Furoperacid, 517
Furunculosis, 769
Fusarium, 711

G acid, 382
Gadolinium compounds, 142
Gaede pump, 148
Gaertner bacillus, 758
Galactose, 432, 433, 521, 752, 883
nitrobenzylidene acetals, 472
Gallacetophenone, 498
Gall bladder, 826
Gallium, in cadmium lamp, 150
Gallocyanine, 632
Galloflavin, 479
Gametes, of *Chlamydomonas*, 767
Gamma-rays, 2, 7, 9
Gas, electrolytic, 310
inert, 77, 131, 132, 138, 296, 297
ionization, 269
irradiation apparatus, 70, 71
natural, chlorination, 526-528
Gas gangrene bacillus, 710
Gasolines, 503, 651, 657, 665
Gastric juice, 677
secretion, 759, 760
Gastrulation, 718
Geelgikup, 861
Geiger-Müller counter, 100, 768
Geissler tube, 30
Gelatin, 363, 481, 620, 645, 662, 676-679, 688, 727
absorption of ultraviolet rays, 7
and cobra venom, 691
and diastase, 682
and lead arsenite papers, 359
and silver nitrate, 383
and silver sols, 388
and Weigert effect, 383
chromate reaction, 365
emulsion, 266, 380
ferric chloride reaction, 384
films, 562, 585, 632
filters, 177, 182, 183-186
gel, 389
in paper, 619
Gels, Liesegang rings in, 391
Gentian violet, 634
Gentianose, 435
Gentiopicrin, 436
Gentisic acid, 479
Geraniol, 514
Geranium, plants, 886
Germane, 333
Germinating layer, of skin, 736
Germination, 716, 849, 885, 886
Getter, 138
Ghee, 856
Glands, of internal secretion, 688, 689, 759, 760
Glass, absorption of ultraviolet rays, 7, 164, 168-176
American Optical Co. Nos. 57 and 58, 165
and drug deterioration, 657, 658
and dye fading, 637, 639
and gasoline color stability, 653
barium, 165, 201
beryllium, 170-172
black, 167, 187
bonding with rubber, 611
Chance's, 100, 187
cobalt, 165, 168
colored, and paper, 620
Corex, 100, 101, 103, 143, 146, 169, 170, 173-175, 179, 181, 185, 325, 637, 653, 704, 781, 843, 844
Corning, 165, 174, 186, 187, 580, 782
Crookes, 164-166
didymium, 177, 178
filters, 164, 177-181, 188, 664, 711, 889
for seals into quartz, 75
for sunlamp, 143, 146
fluorescent, 142, 176, 663
Getan, 172
heat-transmitting, 165
Helio, 174, 175, 181
infrared absorbing, 164
laminated, 167, 411, 591
lead, 148, 165
lime, 165

Glass, lithium, 168, 172
Locke, 174, 175
magnesium, 170
manganese, 176
microscope, 181
neodymium oxide, 178
nickel, 168
Nonex, 75
Noviol, 165, 180, 187, 188, 886
Noviweld, 165
optical crown, 165, 166, 180
phosphate, 132, 133, 168, 172, 176
plate, 176
powdered, in rubber, 610
protective, 164-167
Pyrex, 72, 75, 103, 146
quartz, 173, 175
Schott, 175, 864
sextant, 165
soda-lime, 148, 165, 166, 168, 175, 176
solarization, 174-176
Uviol, 156
Vita, 103, 104, 169, 172-175, 178, 181, 637, 661, 711, 712, 776, 782, 825, 887, 888
window, 103, 169, 170, 173-175
zinc, 165
Glaucobilin, 680
Globin, ammonia formation, 676
Globulin (see Serum globulin)
Glomerella, 890
Glow discharge, 30-32, 47, 93, 131, 136-141, 146
hydrazine formation in, 319
in gasoline treatment, 655
in vitamin D production, 804, 832
nitrogen dioxide synthesis by, 327
Glow lamp, 132, 138-141
Glucolysis, 710, 857, 858
Glucosamine, 433
Glucose, 369, 387, 432-436, 686, 688, 710, 883
and pyridine, 521
fermentation, 709
phenylosazone dicarboxylic acid, 183
photosynthesis, 867
tolerance, 752
Glucosides, 432, 436
Glucuronic acid, 435
Glucuronosidase, 684
Glue, 612, 619
Glutacondialdehyde, ammonia derivative, 519
Glutamine, 883
Glutaric acid, 441
Glutathione, 432, 680, 743, 751, 760, 761, 764, 825
Glyceric acid, 404
aldehyde, 402, 404
Glycerides, 554
Glycerol, 185, 260, 339, 353, 361, 385, 523, 612, 645, 660, 737, 791, 883
from lecithin, 669
oxidation, 404, 559
photolysis, 402, 403
preparation, 407
Glycerol butyl phthalate, 592
nitrobenzylidene benzoyl, 472
phthalic anhydride resins, 585
salicylate, 743
Glycerophosphatase, 818
Glycerophosphoric acid, dehydrogenase, 687
Glycerose, 339
Glycerosone, 431
Glyceryl acrylate, 456
galactoside, 436
Glycine, 260, 671, 672, 677, 681
Glycogen, 436, 706, 742, 752, 753
Glycol, 402, 405, 407, 472, 656
Glycolaldehyde, 404
Glycol, dipropyl, 403
methyl phthalate, 591
nitrobenzylidene, 472
peroxide, 402
salicylate, 743
vinyl ether, 411
Glycollic acid, 451, 671, 867
Glycolysis, and sensitizers, 863
Glycosuria, 752
Glycylglycine, 436, 672
Glycyltyrosine, 436
Glyoxal, 404, 415, 431, 450, 451
Glyoxalic acid, 869
Glyoximes, 461
Glyoxylic acid, 451
Goats, 861
Goitre, 689, 777
Gold, 142, 165, 178, 366, 377
chloride, 371, 391, 522, 605
salts, 359, 388
sol, 388-391, 669, 677
Goldfish, 402
Grains, photographic, 379, 380
Granatum, tincture, 658
Graphite, 253, 341, 612
Graphitic acid, 64
Grass, 790
Grass-bleaching, 615
Grating, diffraction, 4, 6, 7
Grignard compounds, 464
Grotrian diagrams, 27-29
Grotthuss-Draper law, 205, 206
Ground state, 220, 232, 237
Growth, 58, 150, 759, 886-888
Growth-substances in irradiated cells, 708, 709
Guaiacol, 513, 726
Guaiaconic acid, 479
Guaiaretic acid, 479
Guanidine, 458, 672
derivatives, 592, 605, 610, 612
Guanine, 672, 699, 701, 703
Guard cells, of leaves, 715
Guinea Green, 634
Gum, 585, 589
arabic, 363, 387
formation in gasoline, 653-656
in enamels, 590
mastic sol, 387, 390
tragacanth, 612
Gutta-percha, 593-595, 604

H acid, 647
Haber-Willstätter mechanism, 403
Hair, yellowing, 744
Halibut liver oil, 816
Halo-acetic acids, and alcohol, 452
Halogenated acids, 451, 452
Hammerscale, 583
Hanovia lamp, 78, 79, 81, 129, 184, 837 (see also Mercury arc)
Harmonic oscillator, 232, 233, 235
Harteck xenon lamp, 393
Hatchability of eggs, 787, 788
Hausmann numbers, 365
Hay, 790, 817
Hay fever, 776, 824
Heart, 733, 750, 760, 761, 862
Heat of reaction, 245
Heats of dissociation, 217, 235-237, 241, 243, 246, 247
Heavy water, and plants, 882
Hectograph pads, 645
Heimsonne, Alpina, 132-134
Heisenberg uncertainty principle, 236, 243
Helianthine, 631
Helianthrone, derivatives, 506, 507
Helianthus annuus, 882
Helicin, 436
Helioglass, 173-175, 181
Heliotherapy, 733, 734, 770
Helium, 27, 33, 138, 139, 144, 150, 151, 192, 279, 280
effects on various reactions, 273, 296, 327, 329
Hematin, 622, 748, 750
Hematoporphyrin, 263, 264, 671, 673, 678, 749, 751, 852, 860-863, 865
Hemin, 553, 685, 687, 749
Hemochromogen, 690, 750
Hemoglobin, 679, 680, 687, 688, 746, 748, 749, 791
Hemolysins, anti-sheep, 758
Hemolysis, 669, 750, 860, 862, 864, 865
Hemp, 613, 620, 645
Hemsalech coil, 41
Henna, use as protective pigment, 861

Hepatoflavin, 851
Heptachlorocyclohexane carboxyl chloride, 547
Heptane, 394
  iso, 530, 531
Heptylene, 394
Heraeus lamp, 78, 147
Heroine, 726
Herpes, 712, 769
Herschel effect, 256, 380
Herzberg bands, 294, 295
Heteropolytungstic acids, 369
Hexamminecobaltic chloride, 368
Hexachlorocyclohexane carboxyl chloride, 547
Hexachlorodisilane, 64
Hexadecylpyridinium bromide, 644
Hexadiene tetraphenyl, 411
Hexahexosan, 435
Hexahydrobenzene, 211, 466
Hexahydroethylbenzene, 473
Hexane, 182, 393, 394, 429
  chlorination, 526, 530
  nitration, 470
Hexatungstic acid, 369
Hexene, 536
  dimethyl, 461
Hexose, photosynthesis, 868, 870, 878
  phosphates, 432
Hexosephosphatase, 818
Hexuronic acid, 849
Hexyl chloride, 531
Hides, 650, 651
High-frequency field, 36
Hilger monochromator, 190
  spectrograph, 160
  Vitameter, 853
Hippuric acid, 672
Histamine, 672, 673, 677, 733, 740, 741, 749, 759
Histazarin dimethyl ether monoxime, 522
Histidine, 672, 673, 676, 677, 703, 740, 741, 748, 882
Höhensonne lamp, 695
Hofmann violet, 634
Holviglass, 171, 173
Homatropine, 658
Homotropococaine, 436
Hordeum seedlings, 888
Hormones, 688-690
Horn, 678
Hospitals, ultraviolet sterilization in, 728-731
Howland color photometer, 583
Humidity, and dye fading, 636, 641, 642
  and meat tenderizing, 724
  and rayon deterioration, 621
  in accelerated paint tests, 577-579
Humus, 350
Hydantoins, 518, 702
Hydrastinine, 523
Hydrastis, tincture, 658
Hydrates, 437
Hydrazine, 258, 318-323, 363, 371
Hydrazobenzene, formation, 500
Hydrazones, phototropy, 493
Hydriodic acid (see Hydrogen iodide)
Hydroa, 861
Hydrobromic acid (see Hydrogen bromide)
Hydrocarbons, aliphatic, 531
  aromatic, 466-469, 655
  chlorinated, stabilizing, 657
  cyclic, absorption spectra, 651
  formation, 64, 425, 437, 438, 448, 459, 460, 464
  fuels, 652
  in arc, 60
  liquid, 394, 531
  saturated, 393-395, 449, 529
  unsaturated, 393, 438, 449, 531, 533-538, 655
Hydrocellulose, 618
Hydrochloric acid (see Hydrogen chloride and Hydrogen-chlorine combination)
Hydrocinnamaldehyde, 473
Hydrocinnamic acid, 340, 482, 548
Hydrocyanic acid (see Hydrogen cyanide)
Hydrogen, 144, 192, 211, 214, 279, 291, 345, 360, 362, 370, 393, 414, 440, 466, 471, 481, 614, 615, 650, 652
  active, 37
  and dyes, 633
  and ethylene reaction, 406-408
  and gutta-percha, irradiation, 594, 595
  and hemoglobin, 680
  and nitrogen, 318
  and paper, 619
  and rubber, 601
  atomic, 244, 283, 290, 301-305, 309, 310, 313, 316-323, 438, 439, 472, 540, 560, 811, 877-879
  atoms, recombination, 163, 213, 319
  by operating carbon arc under water, 64
  -chlorine combination, 105, 205, 209-211, 213, 218, 244, 246, 253, 255, 281-291, 302, 306, 315
  discharge, 152, 156-162, 208, 270, 698
  dissociation, 163, 229, 231, 237, 272
  effects on various photoreactions, 296, 297, 315, 316, 318, 321, 324, 327, 328, 332, 333, 357, 358, 375, 385, 397, 400, 427, 460, 462, 534, 537, 869
  formation, 339, 349, 396, 398, 399, 402, 406, 416, 417, 420-422, 427, 431, 432, 438-440, 448, 449, 451, 458, 461, 463, 465, 514, 864
  halides, 272-280
  in gasoline testing, 653, 654
  in metal-vapor lamps, 150
  ionization potential, 27
  ortho, 226
  oxidation, 250, 257, 258, 289, 299-305, 310
  para, 226
  reaction with amino radical, 319, 321
  reaction with atomic chlorine, 316
  reaction with carbon dioxide, 308
  reaction with carbon monoxide, 310
  reaction with fluorine, 274
  reaction with iodine chloride, 280
  reaction with nitrous oxide, 325
  reaction with sulfur, 329
  resonance potential, 27
  reduction of sodium molybdate, 369
  spectra, 20-22, 33, 156, 162, 163, 272
  -transferring coenzyme, 688
  zero-point energy, 290
Hydrogen compounds:
  azide, 323, 324, 384
  bromide, 413, 492, 498, 506, 508, 541, 542, 545, 546, 550
    absorption spectrum, 275
    and isostilbene, 548
    photolysis, 211, 212, 272, 274, 275
    photosynthesis, 214, 254, 275-280
  chloride, 187, 315, 346, 366, 369, 508, 527, 528, 530, 531, 537, 539, 544, 546, 548
    absorption spectrum, 239, 281, 343
    and potassium anthraquinone sulfonate, 506
    and pyridine, 518
    and quinine, 523
    dielectric constant, 239
    effect on Cl_2-sensitized chloroform oxidation, 314
    formation, 394, 395, 400, 418, 440, 529, 532, 550
    in reactions of amines, 497
    photolysis, 239, 272, 274, 275, 281
    synthesis (see Hydrogen-chlorine combination)
  cyanide, 62, 363, 451, 456, 458, 498, 875-877, 891
  iodide, 249, 396, 520, 533
    absorption spectrum, 156, 230, 272
    and methyl iodide, 397
    formation, 274, 400, 498, 595
    photolysis, 211, 212, 215, 255, 272-274, 342
    photooxidation, 305
  peroxide, 346, 383, 407, 411, 433-435, 449, 556, 629, 633, 649, 657, 673, 789, 864, 883
    absorption spectrum, 303, 304, 339, 341
    and adrenaline, 688, 689
    and carbohydrate photosynthesis, 868, 876-880
    and *Chlorella*, 875
    and cholesterol, 834
    and dyes, 616, 634
    and hemolysis, 865
    and insulin, 679
    and lethal action of radiations, 695

Hydrogen peroxide (*Continued*)
  and milk irradiation, 722, 840
  and pyridine, 519
  and silver sols, 388
  and soy bean oil, 573
  bleaching by, 618
  dissociation, 304, 339
  emission spectrum, 304
  formation, 299, 300, 302, 339, 604
  in actinometry, 341
  in carbon monoxide oxidation, 309, 310
  in forming metal sols, 387
  in sensitized oxidations, 258, 863
  in water photolysis, 299
  inhibitor of Eder reaction, 445
  oxidations by, 304, 418
  photolysis, 209, 253, 254, 267, 304, 305, 339-341, 410
  reaction with hydroxyl radical, 340
  reaction with oxygen, 340
  sensitizer for ethanol oxidation, 403
Hydrogen sulfide, 354, 359, 367, 390, 407
  absorption spectrum, 329, 336, 355
  and plant photosynthesis, 875
  and vitamin C, 848
  formation, 599, 623, 654
  in paint tests, 580
  photolysis, 329, 330, 355
Hydroquinol, 509
Hydroquinone, 356, 390, 421, 439, 604, 631, 688
  and polymerizations, 410, 595, 596
  formation, 482
  in vitamin D preparations, 833
Hydroxamic acid, 882
Hydroxy acids, 440, 448-450
Hydroxyanthraquinone, 507
Hydroxyazobenzene, 470, 496, 499, 562
Hydroxyazonaphthalene, 503
Hydroxybenzoic acid, 480, 500, 546
Hydroxybiphenyl, sodium sulfonates, 743
Hydroxychlorophyll, 878, 879
Hydroxycholesterol, 792
Hydroxycinnamic acid, 484
Hydroxydimethylaniline, 497
Hydroxydroserone, 502
Hydroxyisatogenic acid, 482
(Hydroxyethyl)isoalloxazine, 852
Hydroxyl ion, absorption spectrum, 338
  radical, 299, 301, 302, 305, 397, 438, 439
    reactions of, 304, 305, 309, 340, 438
Hydroxylamine, 323, 371, 458, 877, 883
Hydroxymethylene camphor, 515
4-Hydroxy-2-methyl-*N*-phenylmorpholine, 612
Hydroxynaphthaquinone, 502
Hydroxynaphthylcrotonic acid, 503
Hydroxynicotinic acid, 702
Hydroxyoleic acid, 553, 559
Hydroxyphenazine, 522
Hydroxyphenylenediamine, 498
Hydroxyphenylpropanolamine, 689
Hydroxyproline, 672, 676
Hydroxyquinoline sulfonic acids, 183
Hydroxysiloxene, 333
Hydroxystearic acid, 560
Hydroxystyrylmethyl ketone, 489
Hyperemia, 734, 741, 746
Hypericum, photosensitizer, 861
Hypertension, therapy, 774
Hyperventilation, 753
Hypnone, 513
Hypobromous acid, 455
Hypochlorous acid, 307, 346, 618
Hypoiodite, 343
Hyponitrous acid, 350
Hypophysis, 690, 790

Illuminating sources, nature of, 15
Imidazoleacetaldehyde, 673
Imidazolylethyl alcohol, 673
Iminodibutyric acid, 455
Immune sera, 706, 757-759
Incandescent lamps, 152, 156
Indanthrene Yellow, 616, 633
Indazole, substituted, 743
Indene, 431, 517
Indicators, fluorescent, 665
Indigo, 616, 622, 633, 638
Indigocarmine, 631, 637, 640, 642
Indigocarmine blue, 634
Indigosol, 632, 645, 647
Indium oxide, 360
Indole derivatives, 517, 671, 743, 887
Indones, 453, 492, 493, 517
Indophenol oxidase, 686
Inductance, 91
Induction coils, 40, 42, 76, 125, 136, 148, 149, 152
Induction period, 205, 253, 255, 434, 441, 532, 540
  acrolein polymerization, 424
  alcohol-benzophenone reaction, 480
  carotene oxidation, 856
  chloroprene polymerization, 596
  cinnamic acid bromination, 486
  Eder reaction, 445
  fat oxidation, 840
  gum formation in gasoline, 655
  hydrogen-chlorine combination, 281, 285-286
  in plant photosynthesis, 871, 872, 877, 881
  in stereoisomerizations, 485, 518
  lactic acid photolysis, 449
  oxidations, 449, 627
  ozone photolysis, 297
  phosgene formation, 311, 313
  succinic acid-methylene blue reaction, 447
  tartaric acid bromination, 541
  vitamin A photolysis, 855
Indulant ulcers, 769
Induline, 634
Infections, 775, 825
Influenza bacillus, 669, 750
  virus, 712, 731
Infrared radiations, 2, 6, 92, 115, 194, 381, 660
  absorption, 165, 220, 222, 224, 225, 235
  effects of, 208, 209, 255, 256, 734
  filters, 178, 183
  in vitamin D production, 828, 832, 840
Inhibition of reactions by light, 255
Inhibitors, 214, 252, 253, 356, 357, 365
  benzaldehyde oxidation, 474
  chloroform chlorination, 533
  hemolysis, 862
  hydrogen-chlorine combination, 283, 285, 287, 302
  hydrogen peroxide photolysis, 340, 341
  of polymerizations, 410
Inks, 641, 644, 645, 648
Inosine, 710
Insolameter, 636
Insulin, 679, 727, 751, 752
Inulin, 436
Intensimeter, 100
Intensity, of light and reactions, 205, 206, 251, 252
Intercombination lines, 29
Interferometer, 4, 5
Interhalogen compounds, 280
Intermediates, in reaction kinetics, 277
Interrupters, 76, 77, 92, 154
Intestinal mucosa, villikinin, 689
Intestine, effects on, 760
Intramolecular electrolysis, 371
Intramolecular migration of energy, 247, 248
Invar, 74
Inverse square law, 692, 771
Invertase, 247
Iodates, 343, 348, 617
Iodide ion, 262-263, 337, 338, 342-344, 363, 439, 681, 684
Iodination of paraffins, 533
Iodine, 187, 359, 371, 534, 550, 648, 680, 745
  absorption spectrum, 230, 235, 237, 272, 273
  action of x-rays on, 209
  and butene, 536
  and catalase, 685
  and formaldehyde photolysis, 422
  atoms, 254, 536, 537
    absorption, 231
    and oxalate ion, 446
    excitation energy, 237-239, 272, 344, 373
    recombination, 273, 446, 536
  decolorized solution, 658

Iodine, dissociation, 273
distribution, 689, 713, 759, 760, 777
effects on photolyses, 399, 535, 536
excited molecules, 274, 536, 537
fluorescence, 231, 272, 273
formation, 342-343, 396-400, 439, 440, 520, 554, 629
heat of dissociation, 237
in discharge tubes, 141
photochemical oxidations, 249, 446, 849
photoionization threshold, 269
photosensitizer, 484, 485, 491, 518, 522, 536, 554, 574
reaction with alcohols, 345, 538
reaction with ferrocyanide, 363
reaction with ferrous sulfate, 344, 345
reaction with formates, 252, 344, 345, 440
reaction with nitrites, 249, 344, 345, 351
reaction with oxalates, 254, 344, 345, 445-447
sorption on cotton, 615
Iodine chloride, 280
green, 634
pentoxide, 399
Iodoacetic acid, 876
Iodoaniline, isodiazotate solution, 646
Iodobenzene, 246, 474
Iodoform, absorption spectrum, 395
action of x-rays on, 209
and cholesterol, 812
oxidation, 253
photolysis, 397, 400
Iodopropionic acid, 439
Iodopsin, 857
Iodopyridinecarboxylic acid, 520
Iodostarin, 554
Iodovinylacetylene, 415
Ionization, atoms, 26, 27, 31, 48, 230
potentials, 27, 372, 379
Ion-molecules, 237
Ionone, 855
Iridium compounds, 360, 415
Iris, 164, 763
Iron, 171, 173, 359, 415
arc, 46, 47, 49, 50, 693
chlorination catalyst, 534
compounds, and paper, 142, 619, 710
corrosion, 661
halides, in polymerizations, 411
ions, 337, 678
irradiated, 748
plates, and aniline, 495
salts, 360-362, 370, 403, 432, 448, 498, 727, 863
spark apparatus, 38, 39, 152, 154
spectrum, 23, 26
Iron acetate, 441
carbide, in carbon arc, 58
carbonyls, 514, 545, 749
chlorides, 514, 545, 749
citrate, 441
mercaptide, 465
mercaptotricarbonyl, 465
naphthenate, 592
oxalate, 441
oxides, 167, 171, 173, 508, 563, 583, 612
porphyrin compound, 685
succinate, 441
tannin compound, 651
tartrate, 441
Irradiated air, and rickets, 788, 789
cholesterol, 791, 826, 847 (see also Vitamin D)
dried milk, 839
ergosterol, 819, 820, 825, 831, 833, 834 (see also Vitamin D)
milk, 789, 841, 844
skin, and rickets, 779
yeast, 789, 837
Irradiation, and resistance to infections, 773, 825
and rickets, 778, 779
apparatus, with filters, 184, 185
lamps, for photochemistry, 139
of foodstuffs, 788-790, 827
of gas, 70
processes, spectrographic control, 833
with restricted wave-lengths, 828
Isatin, 633
Isoalloxazine derivatives, 852
Isoamyl chloride, chlorination, 527
Isoamylamine, 264, 864
Isobutane, 421, 422, 526, 531, 532
Isobutyl magnesium bromide, 464
Isobutylidenecholesterol, 817
Isobutyric acid, 540
Isochlorophylline, sensitizer, 451
Isochromatic plates, 381
Isocinnamic acid, 484
Isocrotonic acid amide, 455
Isocyanine dyes, 381
Isodiazotates, 646
Isoelectric point, 675, 676
Isoergosterol, 796, 797
Isoeugenol, 469, 514
Isoheptane, 530, 531
Isonaphthazarin, 502
Isopentane, 526, 527
Isophotosantonic acid, 516
Isophthalic acid, dihydro, 481
Isoprene, 413, 514, 593-595
Isopropanol, 357, 402-404, 476, 477, 480, 538
Isopropenylmethyl ketone, 429
Isopropyl alcohol (see Isopropanol)
Isopropyl bromide, 399
cyclopentanone, 516
iodide, 396, 398
Isopulegol, 469
Isopulegone, 469
Isopurpuric acid, 498
Isopyrocalciferol, 810-812
Isoquinoline red, 264
Isostilbene, 511, 548
Isotopes, 217, 227
Isouracil, 703
Isovaleraldehyde, 422
Issoglio test, 560
Itaconic acid, 454

Jams, sterilization, 722
Japan wax, light absorption, 586
Jara-jara, 558
Jars, Leyden, 149, 154
Jellies, sterilization, 722
Juglone, 680
Jute, 613, 618

Kala-azar, 777
Kalicrein, 691
Kaolin suspensions, 391
Kaposi's disease, 861
Kauri gum, 585
varnish film, 587
Keratin, 651, 678, 679
Keratoses, 766
Kerosene, 533, 653
Ketene, 428, 430, 431, 440
Keto acids, 393, 451, 562
7-Ketocholesteryl acetate, provitamins from, 817
4-Keto-*N*-ethylphenazine, 522
Ketogluconic acid, 451
Ketohydroxystearic acid, 574
Ketoketenes, 430
Ketone, 393, 464, 476-478, 500, 547
absorption spectra, 415, 416, 425
diethyl, 341, 421, 428
diisoxazole, 517
dimethyl, 341
diphenyl, 595
dipropyl, 429
formation, 450, 657
-furfural resins, 585
isopropenylmethyl, 429
methylbutyl, 421, 429
methylethyl, 341, 421, 429
methylisobutyl, and anisaldehyde, 494
methylpropyl, 429
nitrophenylethyl, 478
phenylnaphthyl, 477
propenylmethyl, 429
photolysis, 421, 425-431
reactions with alcohols, 403, 404, 517
styryl, 489, 493, 494

2-Keto-*N*-methylphenazine, 522
Ketopentose, from formaldehyde, 867
Ketovaleric acid, 451
Ketoses, 432, 869
Khaki, 615
Kidneys, 818, 820, 822
Kieselguhr, 867, 870
Kiton Red, 628
Knop's solution, 887
Koji extract, fermentation, 709
"Kojic acid," 630
Kraft, sulfate, 618
Kromayer lamp, 57, 126, 127, 735, 744, 769, 770, 797
Kreis test, 559, 560
Kryptocyanine, 381

Labarc, 80, 161
Lachesis lanceolatus, toxin, 691
Lacquers, 410, 585, 591
accelerated weathering tests, 586, 587, 590
chlorinated rubber, 611, 612
nitrocellulose, 562, 576, 580, 587
Lactalbumin, 839-841
Lactation, effects of irradiation, 836
Lactic acid, 436, 448-450, 540, 672, 742, 752, 753, 764
acrylic ester, polymer, 456
phenyl, 477, 478, 540
Lactic aldehyde, 518
Lactoflavin, 563, 848, 851, 852
Lactose, 432, 433, 435, 521, 711
nitrobenzylidene acetal, 472
Lakes, 590, 643
Lambert's law, 206
Laminated glass, 411
Lampblack, 583, 659
Lamps (see also Mercury arc)
antimony, 148
bismuth, 148
bulbular, 132
cadmium, 148-150
cathode-ray bombardment, 152, 156
dental, 141
fluorescent, 142, 152
for black light, 179
for exciting luminous paints, 583
gaseous conduction, 132
glow, 132, 138-141
incandescent, 152
lead, 148
Mazda CX, 143
mercury discharge, 131-142
metal-vapor, deterioration, 150
Osram, 68, 175, 539, 640
Philips, 139
positive column, 132, 139
selenium, 148
Sollux, 580
sun, 111, 129, 134, 141, 143-146, 561, 738, 887
tellurium, 148
therapy, 97, 132-134, 138, 139
tubular, 132
tungsten, 156, 173
Uviol, 108, 114, 182
xenon, 151, 300, 308, 393
zinc, 148-150
Lanolin, 563, 743, 792, 813
Lanthanum compounds, 142
Lard, 556, 559, 789
Larvae, 718, 765, 766
Latent image, 373, 374, 376-381
Latex, 593, 594, 596, 597
Lattice, crystal, 372-374, 385
Lauth's violet, 263, 631
Lavender oil, 513
Lead, 150, 172, 464, 661
and fatty acids, 554
driers, 572, 573
excretion, 760, 825
glass, 165
ion, 377
lamp, 158
poisoning, 825
reduction scale, pigment, 583
Lead, seals, for mercury arc, 74, 75, 80
sols, 386
spark, 155
Lead abietate, 558
acetate, 184, 613, 616, 726
arsenite, 358, 359
carbonates, 577, 583
chromates, 391, 608, 615, 616
hydroxide, 386
oxide, 168, 360, 481, 630
peroxide, 253, 341
phthalate, 481
picrate, 354
tetraethyl, 464, 657
tetramethyl, photolysis, 464
tetraphenyl, photolysis, 464
Leather, 293, 645, 650, 651
Leaves, plant, 498, 715, 866, 886
Lecithin, 669, 750, 766, 834
Leg weakness, 202, 782, 786, 787, 813, 814
Lemon juice, reducing agent, 849
oil, 513
Lens, of eye, 164, 762-764
Lentil seeds, 716, 885
Lepidine, 508, 521
Lethal action, of ultraviolet rays, 193, 247, 692-707, 716
Lettuce, irradiated, 830, 889
Leucine, 671
Leucobases, of triphenylmethane dyes, 627, 628
Leucocytes, 746-748, 751, 756, 759
Leucomethylene blue, 263, 264, 630, 631
Levulinic acid, light absorption, 451
Levulose, 432, 433
Leyden jars, 149, 154, 292
Licanic acid, 574
Liebermann's polyester, 484
Liesegang rings, 391, 392
Light, as inhibitor of reactions, 255
as limiting factor in photosynthesis, 873
complex, additivity of effects, 442
nature of, 2, 3, 4, 6
polarized, 4, 435, 442, 882
Light-fastness of dyes, 634-642
Lighting, fluorescent, 142
Light-stroke, 860
Lignin, 550, 617, 620
Limax flavus, embryos, 718
Lime, 168, 169, 171, 172, 179
Lime blossoms, 657
Linen, 188, 205, 615, 618, 620, 645, 646
Lines, Balmer, 156, 163
enhanced, 32, 33
forbidden, 92
intensities and origins, 106
intercombination, 29
mercury, 65, 67, 92, 115, 116, 188
physical isolation, 189, 190
resonance, 136, 137, 141, 150, 151
reversed, 109, 110, 152
spectral, width of, 243
Linoleic acid, 553, 554, 558, 564, 567
Linolenic acid, 553, 554, 567, 570
Linoleum, 573, 574, 727
Linolic acid, 570
Linseed oil, 557, 565, 613, 650
absorption spectrum, 555, 568-571
and lithopone blackening, 386
bleaching, 568, 573
bromination, 567-569
drying, 567-570, 572, 574
in sterilization, 727
irradiated, 789
oxidation, 558, 559, 569
products from, 573
Lipase, 680, 683, 742, 756
Lipid phosphorus, in cancer tissue, 766
Lipids, 669, 670, 727, 883, 887
Lipochrome, 559
Lipoid peroxide, in plant photosynthesis, 876
Liquids, photoreactions in, 335-336
Litharge, in rubber, 610
Lithion carmine, 634
Lithium bromide, 239, 344
carbonate, 172

Lithium chloride, 390, 681
fluoride, prisms, 7
halides, 239
iodide, 239, 372, 373
nitrate, 479
Lithographic inks, testing, 641
Lithol red, barium salt, 643
Lithopones, 575, 590, 600, 743
actinometer, 104, 105
and vulcanization, 599
blackening, 384-386, 580
in rubber, 610
light absorption, 582, 583
paints, accelerated tests, 577, 580
photoconductivity, 385
Liver, beef, antirachitic substance, 817
calcification, 820
catalase, 685, 756
extracts, 630, 686
glycogen, 753
inorganic phosphorus, 818
of irradiated animals, 789
oil, absorption spectrum, 854
oxygen consumption, 825, 826
Locke's glass, 174, 175
Lovibond scale, 165, 642
Lubricating oil, 557, 652, 653
Lumichrome, 851, 852
Lumiflavin, 851, 853
Luminescence, 265, 375, 559
analysis (see Fluorescence analysis)
Lumisterol, 807-812, 816
Lupus, 742, 769
Lyman region, 7
series, 21, 22
Lymph, 751
Lymphocytosis, 746
Lymphoid tissue, 759
Lymphopenia, 746
Lysin, 759
Lysine, liberation of ammonia, 672, 677
Lysis, of irradiated cells, 704

Mace oil, absorption spectrum, 513
Macronuclei, 703
Macrosporium tomato, 711
Madder lakes, 590
Magenta, 634, 642
Magnalium mirror, in discharge tube, 142
Magnesia, 168, 360, 582, 583
Magnesium, 171, 760
Magnesium carbonate, 176, 583, 609, 868, 869, 878
chloride, 361, 704
discharge lamps, 141, 142
flashes, 290
glass, 170
hydroxyazonaphthalenedisulfonate, 502
in blood, 754
in plants, 889
lines, temperature classification, 26
nitronaphthalenesulfonic acid, 502
of skin, 742
peroxide, 573
phosphates, 172
resinates, 585
spark, 795, 797-799, 801, 808, 816, 834
sulfate, 440, 890
underwater spark, 155
Magnetic susceptibility, 294
Mahua oil, oxidation, 559
Maize oil, 560, 563
Malachite green, 265, 350, 498, 592, 595, 627-629, 634, 639, 868, 869
Malaria, 776
Maleic acid, 211, 407, 412, 452-454, 455, 457, 541, 621
anhydride, 453, 806, 834
Maleonitrile, 457
Malic acid, 361, 445, 518, 660, 672, 764, 884, 891
Malonic acid, 440, 441, 447, 523
anhydride, 447
Malpighian layer, of skin, 734, 735
Malt-agar medium, irradiation, 708
Malt, 681, 682, 722
Maltase, 681
Maltoflavin, 851
Maltose, 432-434, 436
Mammary glands, irradiation, 754
Mandelic acid, 448-450, 481, 540
Manganese, abietate, 558
and cotton, 617
and fatty acids, 554
and lithopone blackening, 385
cations, absorption spectra, 337
chloride, 434, 456, 545, 870
complex cyanide, 363
driers, 572
in carbon arc, 57
in glass, 168, 176
in plants, 889
lines, temperature classification, 26
oxides, 165-167, 171, 176, 863
salts, 187, 353, 370, 409, 498, 727
sulfate, 364
Manganic hydroxide, 363
Manila resin, 585
Mannitol, 383, 403, 472
Mannose, 432, 472, 883
Margarine, 556
Marine organisms, irradiation of, 717, 718
Mass, action and photochemistry, 206
reduced, 224
spectograph, 227
Mastitis, 777
Material, selvedge-resistant, 621
ultraviolet-transmitting, 172-176
Maxwell-Boltzmann law, 245
Mazda lamps, 143, 889
Mead, aging, 660
Meadow-lane, transmission by, 188
Meal worm chrysalids, 744
Mean critical tone, of dyes, 635
Meat industry, ultraviolet radiation in, 724
Mechanism, of photochemical processes, 205-216
Media, bacteriologic, 694, 695, 698, 712, 716
Medicinal products, sterilization, 725-728
Meesemaecker reaction, 796
Melanin, 671, 684, 739, 740, 890
formation, 671, 684
Melanoblasts, 671
Melesitose, hydrolysis, 435
Mellon Institute, air pollution studies at, 98
Membranes, collodion-lecithin, 669
formation by eggs, 717
Menhaden oil, drying, 574
Meningococcus, 696
Menthol, and acetone, 514
Menthyl derivatives, 404, 453, 743
Mercaptans, 463, 654
Mercaptides, in petroleum products, 652
Mercaptobenzothiazole, 600, 605
Mercerization, 616
Mercuric acetate, 541
bromide, 455
chloride, 205, 267, 366, 367, 371, 444, 445, 705
iodide, 367, 391, 812
nitrate, 364
oxide, 302, 367, 371, 502, 630, 883
sulfate, 439
sulfide, 384, 391
Mercurochrome, 658
Mercurous bromide, 105
chloride, 105
iodide, 399
nitrate, 455
sulfate, 367
Mercury arc, abnormal, 82
absorption by mercury within, 107, 109, 110, 115, 117, 118, 121, 124, 132, 136, 141, 144
accessories, 81
alternating current operation, 91, 92
aging, 100, 102, 104, 117, 127-130
anode processes in, 81, 85
anodes, 73, 74, 80
as polariscope source, 68
as radiation standard, 99, 100
carbon anode, 74
cathode processes in, 32, 79, 81-83, 93
cleanup of mercury in, 84

Mercury arc, commercial, 72, 78
constricted, 64, 65, 68, 84, 87, 88, 115, 119-124, 129, 130, 190
Cooper-Hewitt, 100, 107-114, 131, 143, 150, 158, 693, 789
deposits in, 129, 130
distribution of mercury in, 73, 75, 78-80, 84
effect of arc current, 84, 106, 108, 114, 115-117
effect on glass, 175, 176
effects of irradiation by, 615, 650, 681, 682, 694, 696, 701, 731, 734, 744, 745, 748, 770, 778, 779, 784, 787, 824
effect of pressure on, 77, 84
effect of temperature on, 86-89, 117
electrical characteristics, 79, 81, 84-90
electrodes, 73, 74, 80, 133, 137
electromagnetic deflection of, 118, 119, 122
explosion of, 124
Fischer, 69
for 3650 A., 179
for forming ozone, 68, 69, 292, 293
for photochemistry, 68-73
General Electric Vapor Lamp Co., 131
green line, 177, 178
Hanovia, 79, 129
Heraeus, 78, 147
high pressure, 68, 72, 78, 80, 81, 84
history of, 65, 66
Hulburt, 72
instability, 77, 87-90
iron anode, 69, 75
K.B.B., 104
Kromayer, 57, 126, 127, 735, 744, 769, 770, 797
Labarc, 80, 161
laboratory-built, 68-72
leads, 74, 75, 78-80
low pressure, 80, 81, 86, 87
measurement of line intensities, 103
molybdenum in, 79, 80, 83
operated on lighting circuit, 75
pole vessels, 79
pressure in, 77, 79, 80, 84, 87, 94
Pyrex windows, 72
radiating fins, 73, 79
regulation, 88-90
resistance for, 81
R.U.V., 107
seals, 72, 74, 75, 80
spectral energy distribution, 34, 77, 78, 87, 94-97, 106-117, 141, 157, 195
starting, 68, 69, 73, 74-77, 79, 91, 92
strengthening, 78
temperature of electrodes, 73, 74, 78-80
theory, 81-95
tungsten anode, 79, 80
uses, biological, 71-73, 81, 771
uses, industrial, 578, 580, 581, 607, 618, 635, 636, 638-640, 643, 656, 719, 720, 723, 799
Uviarc, 80, 81, 85-87, 89, 92, 100, 117, 129, 134-137, 174, 175
variation of output after striking, 116, 117
Victor, 701
water-cooled, 73, 78, 80, 86-89, 124-127
Weigert, 71
Mercury-argon discharge, for milk irradiation, 840
Mercury, attempted conversion to gold, 366
cathode, irradiated, 339
compounds, 142, 268, 367
dimethyl, photolysis, 464
discharge lamps, 131-142, 654, 655, 723, 842
effect on sulfur dioxide photolysis, 330
emission bands, 92, 94, 95
energy-level diagram, 27-29, 92
excited, 93, 231, 257, 258, 295, 302
formation, 464
fluorescence quenching, 257
fulminate, 367, 463
glow discharge, 93
halides, 367
hydride bands in S-1 sunlamp, 144
interrupter, 154
ionization potential, 27
isotopes, 227
lines, 28, 92, 93, 144, 146
metastable, 92, 93, 257, 258, 322
Mercury, molecule, 95
nitrate, 353
oxide, and cholesterol, 812
phthalate, 481
purification, 124
reaction with methyl iodide, 399
reasonance lines, 8, 27, 29, 92, 117-124, 127, 257, 800, 829
sensitization by, 257, 258, 301, 304, 305, 466
sulfides, 367
toxicity, 124
-vapor arc, 65-97
Mesaconic acid, methyl, 456
Mesidine, 647
Mesitylene, oxidation, 468
Mesityl oxide, 429, 461, 494
Mesophyll, in irradiated plants, 715
Metabolism, basal, 744-746, 825, 826
carbohydrate, 751-753
Metal carbonyls, 464
Metaldehyde, 418
Metals, and fatty acids, 554
and ergosterol, 832
and lacquer yellowing, 592
and lithopone blackening, 384, 385
and stability of trinitrotoluene, 472
bonding with rubber, 611
corrosion, 661
deposition, 359
irradiated, 563, 728
in liquid ammonia, photoreaction, 349
in plant photosynthesis, 878
oxides, 58, 472
particles, in preservative wrappers, 562
salts, as photosensitizers, 862
sols, preparation, 386, 387
vapor arcs, non-mercury, 147-151
Metastable state, mercury, 92, 93
Metastases, of sarcoma, 766
Metastyrene, 488
Metatungstic acid, 369
Meter, ultraviolet, 97-100
Methacrylates, polymerization, 584
Methane, absorption spectrum, 393, 394
chlorination, 395, 526-529, 532, 533
chlorine-sensitized oxidation, 394, 395
decomposition by sparks, 45
diiodo, 400
effect on ethyl diazoacetate photolysis, 460
formation, 258, 394, 396-398, 407, 416, 418, 420, 425, 427, 428, 431-433, 438, 448, 458, 459, 461, 464, 480
photolysis, 240, 393
reaction with acetylene, 415
reaction with iodine chloride, 280
sensitized reaction with deuterium, 394
Methanol, 433, 439, 455, 533, 882
absorption spectrum, 401, 402
formation, 397, 433
oxidation, 402, 404
photolysis, 231, 402
removal of metal carbonyls, 464
Methemoglobin, 680, 863
Methoxyaniline, 497, 498
Methoxybenzophenone, 477
Methoxybenzoylacrylic esters, 491
Methoxycinnamic acid, 483, 487
Methoxycinnamylideneacetic acid, 485
Methoxyethoxysalicylaldehyde, nitration product, 476
Methoxymethylphthalate, 592
Methoxyl group, effect on coumaric acid transformation, 488
Methoxyquinoline, 521
Methoxy, phenylfluorenethioglycollic acid, 511
Methyl acetate, and sulfite oxidation, 356
Methylacetylene, polymerization, 415
Methylacrylonitrile, polymerization, 457
Methylal, 397, 416
Methyl alcohol (see Methanol)
Methylalloxazine, 852
Methylamine, 322, 408, 458, 522, 523, 883
2-Methyl-5-aminopyridine, 520
Methylanisylacrylic acid, 491
Methylanthracene, 505, 509

Methylanthrahydroquinol carboxylic lactone, 507
Methylanthraquinones, 506, 617
Methylarbutin, 436
Methylazoxybenzene, 496
Methyl benzalpyruvate, 491, 492
Methyl benzoate, 340, 480
Methylbenzophenone, 477
Methylbenzoylacrylate, 491, 492
3-Methyl-6,7-benzoylene-benzopyrrole, 518
Methyl-4-benzylidene-3-methylhydantoin-1-acetate, 518
Methylbenzyl oxide, 595
Methyl bromide, 395, 396
Methyl bromo-5-bromo-2,4-dimethoxybenzoylacrylate, 491
Methylbutyl ketone, 421, 429
Methylchalcone, 490
Methyl chloride, 394-396, 526-529, 532
Methyl chloroformate, 539
Methyl chloromethylsulfate, formation, 538
Methylcholanthrene, 765
Methyl cholate, 670, 817
Methylcinnamide, 484
Methylcoumaric acid, 488
Methyl cyanide, dissociation, 231
Methylcyclohexanone, 516
Methylcyclopentanone, 516
4-Methyl-2,6-dianisal-1-cyclohexanone, 517
Methyldihydrochalcone, semicarbazone, 491
Methyl diphenylmaleate, 454
Methylene aminoacetonitrile, 612
Methylene blue, 182, 259, 265, 599, 629-631, 633, 686
  and chlorophyll, 873
  and irradiated skin, 742
  and oxidation of oils, 558
  and plasma oxidation, 678
  and rubber gelation, 595
  and textiles, 614, 617
  and vaccine virus, 712, 713
  bleaching, 263, 630, 640
  filter, 744
  in actinometry, 102, 103, 105
  oxidation of mandelic acid, 449, 450, 481
  reduction by ascorbic acid, 849
  reduction by milk, 761, 762
  reduction by pyruvic acid, 451
  sensitizer, 498, 862
  -succinic acid reaction, 447
Methylene chloride, 394-396, 528
Methylenedioxychalcone, 490
Methylenedioxy-*syn*-aldoxime, 494
Methylene green, actinometer, 105
  iodide, 398, 399
  radicals, 430
Methylene-*p*-toluidine, 610
Methylene violet, 265, 629
Methylethylcarbinol, 404
Methylethylene, formation, 429
Methylethyl ketone, 421, 429
Methyl formate, 439, 539
Methylfluorene, 490
Methyl fumarate, 455
Methylgalactose, nitrobenzylidene acetal, 472
Methyl halides, 440
2-Methyl-3-hydroxy-4,5-di(hydroxymethyl)-pyridine, 850
Methylindigo, 616
Methylindole, 517
Methyl iodide, 244, 246, 395-399
Methylisatin, 616
9-Methylisoalloxazine, 852
Methylisobutyl ketone, 494
Methylisopropylacetaldehyde, 809
Methyl-γ-ketopentadienedicarboxylate, 489
Methyl laurate, oxidation, 559
Methyl maleate, 455
Methyl mercuric iodide, formation, 399
Methylmesaconic acid, 456
Methyl methacrylate, 584, 596
Methyl(4-methylphenyl)(*p*-ethylphenyl)trimethylmethane, 267
Methylnaphthaquinone, 502
Methylnaphthoxazole, 743
Methylnaphthopyrone, 502, 503
Methylnaphthoyl chloride, 549
Methyl nitrite, photolysis, 460, 461
o-Methyl-3-nitro-4-methoxybenzaldoxime, 494
Methyl-*o*-nitro-*o*-methoxycinnamate, 483
o-Methyl-6-nitro-3,4-methylenedioxybenzaldoxime, 494
Methyl orange, 382, 622, 868
Methyl oxalate, 340
Methylphenazonium salts, 522
Methyl phenoxybenzoylacrylate, 491
10-Methyl-9-phenylanthracene, photoöxide, 508
Methylphenylglyoxime, 461
Methylphenylindone, 493, 517
Methylphenyltetrachloroarsine, 549
2-Methyl-1,3-propane diol, 833
Methylpropyl ketone, formation, 429
Methylpyridines, 519
Methylpyridones, 261
Methylpyridinium salt of 1,8-nitronaphthalenesulfonic acid, 502
Methyl radical, 393, 397, 398, 417, 420, 421, 427-430, 438, 459, 460, 464, 529
Methyl red, chlorophyll-sensitized reduction, 625, 626
Methyl salicylate, 481
Methyl stearate, 541
Methylstyryl ketone, semicarbazone, 494
Methyl sulfate, 538
Methyl truxillate, 484
Methyl violet, 179, 259, 260, 634, 639, 640
Methylumbelliferone, 621
Methyluracil, 698
Mica, filters, 188, 694
Mice, sensitization to light, 751, 860
Micelles, silver, 383
Michler's ketone, 477, 629
  diethylmercaptol, 626
Microscope, fluorescence, 651, 665
Migration, electrophoretic, 387, 388
  in N-substituted amines, 496, 497
  of O atom from nitro group, 471, 472, 474-476, 516
Milk, and methylene blue, 761, 762
  antienzymes, 840
  destruction of vitamins of, 848, 854
  flavin assay, 852
  film capacity, 841, 844, 846
  flavor, 563, 829
  irradiation, 721, 761, 785, 789, 793, 827, 829, 831, 835-846
  oxidation-reduction potentials, 761, 762, 849
  protection from light, 563
  provitamin content, 841
  secretion, 761, 785, 836
  sterilization, 721, 722
  xanthine oxidase of, 686
Millimicron, 5
Mineral oil, 555, 600, 610, 619, 651, 652, 727, 743, 789
  rubber, 610
Minerals, fluorescence, 178, 664
  spark spectra, 42
Mint tablets, accelerated testing, 513
Mirror test, atomic hydrogen, 429, 438, 439
Mitogenetic rays, 101, 150, 767, 768
Mitosis, distribution of nucleic acid, 704
Mohair, fluorescence, 645
Moisture, and Budde effect, 282
  and cotton deterioration, 614
  and textiles, 613
  effect on hydrogen-oxygen combination, 299
Molds, irradiation, 659, 694, 711, 723, 724, 828, 831, 838
Molecular electrolysis, 259, 260, 339
Molecular orientation, and photoreactions, 265
  spectra, 217-228, 230, 231, 234, 235
Molecules, antisymmetrical, 226
Molecules, diatomic, band spectra, 218-223, 230
  excited, 212, 214-216, 218, 226, 229, 242, 251, 262, 264
  heteropolar, 221, 237-240
  homopolar, 221, 222, 224, 226-240
  polyatomic, 231, 241, 244
  symmetrical, 221, 226
"Moleoxides," of oils, 558

Molybdenum, 58, 74, 79, 80, 83, 149, 369
  chlorides, 545
  oxides, 152, 244, 354
  spark, 154
"Molybdenum indigo," 244
Molybdic acid sol, 369
Moment of inertia, 222, 225, 227
Monarda fistulosa, essential oil, 513
Monoalkymalonic acids, 447
Monobromobenzene, 543
Monobromomethylanthraquinones, 506
Monobromophenylcyclopropane-1,2-dicarboxylic acid, 541
Monobromopinacolone, 539
Monobutyrin, 436
Monochloracetic acid, 104, 401, 451, 452, 540, 594
Monochlorocineole, 550
Monochlorohexamethylene, 531
Monochlorohydrocarbons, 531
Monochloroisoheptane, 530, 531
Monochloromethane, 529
Monochloromethylanthraquinone, 506
Monochloropinacolone, 538, 539
Monochromators, 96, 190, 696, 782, 800, 808
Monodehydrochlorophyll, 878
Monoiodopentachlorobenzene, 544
Monomolecular films, proteins, 676, 677
Mononitromethylanthraquinones, 506
Montan wax, in rubber, 610
Mordant, copper compounds, 645
  dyes, fading, 635, 642
Morphine, 525, 726, 741
Mosquito larvae, 765
Mother-of-pearl, 165
Mt. Wilson, solar energy at, 199
Muconic acid, 484
Multiplicity, in spectral series, 24, 25
  of molecular states, 225, 226
Multiplets, 24
"Multiple-hit-to-kill" relation, 705, 707, 708
Muscle, 753, 760, 761, 818, 820, 862
Mushrooms, irradiated, 831
Mustard, 886
Mustard oil, 513, 559
Mutarotation, and circularly polarized light, 435
Mycelia, of fungi, 711, 889
Mylius reaction, 670

Nainsook, 189
Naja tripudians, toxin, 691
Nakagawa reaction, of bile acids, 669
Naphthacenes, 509-511
Naphthadianthrone, dimethoxy, 507
Naphtha dyes, 643
Naphthalene, 183, 414, 469, 471, 501-503, 507, 508, 549, 591
β-Naphthaleneazo-β-naphthol, 503
Naphthalene, azoxy, 493
  blue, 634
  chloro, 549
  diamino, 497
  1,5-dibenzoyl-2,6-dimethyl, 549
Naphthalene,1,5-di(*o*-chlorobenzoyl), 549
  diazonium chloride, 625
  nitro derivatives, 501
  β-tetrachloro-α-keto, 493
  tetrahydro, 613
Naphthaquinones, 502
Naphthenes, 655
Naphthionic acid, 382
Naphthobianthrone, 506
Naphthol, 469, 471, 646, 659, 863
  acyl derivatives, 647
  dyes, 634
  Green, 632, 634
  sulfonic acids, 382, 390, 643, 743
  Yellow, 643
Naphthophenazine, 626
Naphthoquinone, 507, 603
Naphthoxazole, methyl, 743
Naphthoyl chloride, 2-methyl, 549
Naphthylaldehyde-1-carboxylic acid, 549
Naphthylamine, 382, 497, 515, 519, 575, 646
Naphthylamine sulfonic acids, 382
Naphthylaminocamphor, 268, 515
Naphthyliminocamphor, 516
Narcotics, and plant photosynthesis, 875, 876
Narcotine, 849
Natural gas, chlorination, 526-528
Natural Green, 638
Naval powders, 462
Necrobiotic rays, 768
Negative branch, 223
Negative glow, 30, 31, 132, 138-140
Nencki's hematoporphyrin, 751
Neoarsphenamine, 759, 776
Neocyanine, 381
Neodymium oxide, 19, 178
Neolan Green, 640, 642
Neon, 27, 136, 138, 144
Neon-argon discharge tube, 722
Neoplasms, 766
Neoprene, fluorescence, 601
Nernst glower, 34
Nerves, 733, 862
Nervous control, effects of irradiation, 734, 740, 746
Neutral red, 631
New Brunswick, solar energy at, 195
"Newglass," 175
New Orleans, solar radiation at, 202
Newsprint, 619
Nickel, 166, 168, 169, 334, 415
  cations, absorption spectra, 337
  electrodes, 131, 138, 160, 161
  in cored-carbon arc, 55
  leads for mercury arc, 78, 79
  lines, 26, 238
  rods, 148
  salts, 187, 359, 370, 409
  sensitizer, 265, 354, 554, 617, 832
  spark, 154
Nickel carbonate, 268, 869, 870
  carbonyls, 331, 333, 334, 465
  chloride, 187
  hydroxide, 368
  oxide, 132, 179, 368, 663, 685, 870
  sulfate, 186, 359
Nicol prism, 270
Nicotine, 521-523, 883
Nicotinea glutinosa, 712
Nicotinic acid, 523, 703, 850
Night blindness, 858
Nigrosin, 634
Nile blue, 264, 498, 631, 634
Ninhydrin, and wool, 622
Nitra lamp, 580, 703
Nitraniline, 497, 558
Nitrate ion, electron-affinity spectrum, 337
  photolysis, 211
  reduction, 102, 104, 259, 353, 354
Nitrates, 102, 171, 193, 322, 350-353, 523, 883
Nitrations, 469, 470
Nitre, 165
Nitric acid, 193, 351, 352, 407, 469, 479, 518
Nitric oxide, absorption spectrum, 160, 324, 325, 326
  and aldehyde photolysis, 421, 422
  and dyes, 633
  effect on various photolyses, 326, 327, 460, 464
  formation, 51, 304, 351, 364, 461, 462, 475
  inhibitor of hydrogen-chlorine combination, 285
  photoionization threshold, 269
  photolysis, 325, 326
  reaction with carbon monoxide, 310
  reaction with cyanogen, 58
Nitrides, 58, 139
Nitriles, 458
Nitrites, absorption spectrum, 351, 461
  and formaldehyde, 882
  and hydrogen peroxide photolysis, 341
  formation, 259, 322, 350, 352, 458, 523, 869, 883
  in atmosphere, 193
  in soil, 350, 351
Nitritoammine cobalt compounds, 368
Nitroamines, and textiles, 499
2-Nitro-4-amino-α-naphthol-7-sulfonic acid, 643
Nitroammine cobaltic chloride, hydrolysis, 368
Nitroanilines, 495, 519

Nitroanisole, 592
Nitroanthracene sulfonic acids, 502
Nitroanthraquinonesulfonic acids, 506
Nitrobenzaldehyde, 472, 474-476
Nitrobenzaldoximes, methyl ether, 493, 494
Nitrobenzalpentaerythrito-1-spiran, 516
Nitrobenzene, 188, 467, 482, 496, 510, 592
Nitrobenzenedisulfide, 501
Nitrobenzenesulfonic acids, 501
Nitrobenzodimethylamidoxime, 494
α-o-p-Nitrobenzyl ethers, of aldoximes, 494
Nitrobenzylidene acetals, 472
o-Nitrobenzylideneglycols, 472
Nitrobromostyrene, 489
Nitrocamphor, 515
Nitrocellulose, 354, 462, 463, 588
  films, 585, 588, 589, 650
  lacquer, 562, 576, 580, 583, 587
  photolysis, 589, 592
Nitrochalcones, 490
Nitrocinnamaldehyde, 475
Nitrocinnamic acid, 482
Nitrocobaltic compounds, 260
Nitro compounds, 460-463, 469-472
2-Nitro-4′,4″-diaminotriphenylmethane, 626
Nitrodimethylaniline, 497
4-Nitro-2,6-dinitrosodihydroxymethylbenzene, 471
Nitro dyes, 640, 643
Nitrogen, 144, 156, 279, 345, 422, 468, 470, 471, 523, 650
  absorption, 181, 193, 317
  active, 37
  and anthraquinone, coloration, 506
  and dyes, 626, 633
  and egg albumin, 678
  and hydrogen, 318
  and insulin irradiation, 679
  and peptides, 674
  and pheophorbide, 879
  and rubber, 593, 595, 601, 602
  compounds, photochemistry, 317-329
  discharge in, 137, 139
  effect on chlorination of acetylene, 537
  effects on various photoreactions, 296-298, 305, 309, 316, 318, 321, 327-329, 331, 358, 400, 401, 426, 428, 435, 436, 460, 462, 475, 537, 545
  fixation in soil, 350, 351
  for irradiation, 184
  for lamps, 583
  formation, 64, 351, 384, 456-462, 498, 500, 515, 624, 625
  glow discharge, 30, 31
  heat of dissociation, 235
  in gasoline testing, 653, 654
  in metal-vapor lamps, 150
  ionization potentials, 27
  isotopes, 227
  metabolism, 745, 746
  organic compounds and light-fastness of pigments, 575
  oxidation, 324
  photoionization threshold, 237, 269
  predissociation, 242
  resonance potentials, 27
Nitrogen dioxide, 247, 327, 371
  iodide, 354
  oxides, 193, 194, 240, 324-328, 733
  pentoxide, 210, 327, 328, 354
  peroxide, 304, 324, 457, 469, 470, 521
  predissociation, 241, 243, 244, 326, 327
  trichloride, 285, 329
  trioxide, 515
Nitroglycerin, 354, 461, 462
Nitro group, 488, 516
Nitromethoxybenzaldoximes, 494
5-Nitro-2-methoxy-3-ethoxybenzaldehyde, 476
Nitromethylnaphthalene, 502, 549
Nitronaphthalene, derivatives, 501, 502, 549
Nitro-nitroso-hydroxymethyl-benzoquinone-oximes, 471
Nitroparaffins, 461
Nitrophthalide, 548
Nitrophthaldehydic acid, 548
Nitrophenols, 499
Nitrophenylethyl ketone, 478
Nitropiperonal, 515
Nitro-rayon, 613
Nitrosobenzaldehyde, 475
Nitrosobenzene, 469, 470, 496
Nitrosobenzoic acid, 472, 474, 475, 516
Nitroso compounds, oxidation, 461
Nitrosodimethylamine, 382
Nitrosodimethylaniline, 178, 179, 182, 495, 497
Nitrosodimethylhexane, 461
Nitroso dyes, 640
Nitrosoisopropyl acetone, 461
Nitrosonaphthylhydroxylamine, 503
Nitrosoterephthaldehydic acid, 476
Nitrosulfonic acid, 546
Nitroterephthaldehyde, 476
2-Nitro-3,4,2′,5′-tetramethoxy-α-phenylcinnamic acid, 484
Nitrotoluenes, 467, 469, 472, 496, 502
Nitrotriphenylmethane, 626
Nitrous acid, 351, 498
  organisms, of soil, 351
  oxide, 285, 324, 325, 327, 397, 461, 462, 633
Nitrosyl chloride, 328, 329, 460, 470
Nitzschia closterium, 790
Nonachlorocyclohexane, 543
Nonex glass, 75
Northrop-Kunitz electrophoresis cells, 704
Nostoc, 883
Novarsenol, 776
"Noviol," 165, 180, 187, 188, 886
Novarsolan, 776
"Noviweld," 165
Novocaine, 740
Nuclei, formation in air, 387
Nucleic acids, 690, 696, 698, 700-703, 712, 716, 850
Nuclein phosphorus, 766
Nucleins, irradiated, 703
Nucleoproteins, 696, 712
Nucleus, of cell and lethal action, 696
Number, atomic, 21
  quantum, 21, 22
Nursing mothers, irradiation, 785

Oak bark, extract, 743
Oats, 886, 887
Octachlorobutane, formation, 401
Octachlorocyclohexene, 543
Octane, formation, 394
Octoic acid, 559
Octyl alcohols, 658
Octylaldehyde, absorption spectrum, 416
Oil, almond, 743, 513
  bergamot, and sunburn, 743
  cacao, 556
  cade, 513
  candlenut, 574
  cassia, 513
  castor (see Castor oil)
  Chinawood, 564-567
  cinnamon, 513
  clove, 513
  cocoanut, oxidation, 559
  cod-liver (see Cod-liver oil)
  colza, 559, 612
  corn, 557, 574
  cottonseed (see Cottonseed oil)
  dogfish, 853
  eucalyptus, bleaching, 513
  fish-liver, 555, 853
  lavender, 513
  linseed, 555, 557, 565, 613 (see also Linseed oil)
  lemon, absorption spectrum, 513
  mace, 513
  Mahua, oxidation, 559
  maize, 560, 563
  menhaden, drying, 574
  mineral (see Mineral oil)
  Monarda fistulosa, 513
  mustard, 513, 559
  oiticica, 574
  olive (see Olive oil)

Oil, palm, 556, 610
  peanut (see Peanut oil)
  peppermint, 513
  perilla, 567, 571, 573, 574
  petroleum, 651
  pilchard, 574
  pine, 610, 659
  plant, activated, 815
  poppyseed, 567, 571, 572, 574
  rat liver, 854
  Red S, 610
  rubberseed, 574
  sassafras, 513
  sesame, 559
  shale, 865
  shark-liver, 855
  solar, chlorination, 531
  Soluble Red O, 659
  soybean (see Soybean oil)
  sunflower, 571, 574, 790
  Telfairia, 574
  thyme, 513
  transformer, 561
  tsubaki, 559
  tung (see Tung oil)
  Turkey red, 613
  turpentine, 513, 514, 610
  vegetable, 555, 557, 610, 612, 789
  whale, 555, 557
  wintergreen, 513
  wormseed, 513
Oils, aging, 589
  drying, 205, 531, 564-574
  essential, 513, 727, 728
  fluorescence, 555, 556, 600
  formation in plants, 882
  hydrogenation, 558
  irradiation, 727, 728, 827
  lubricating, 557
  oxidation, 558, 572
  polymerization, 564-566
  sensitizing ultraviolet photography, 381, 556
  staining fabrics, 624
  stereoisomeric changes, 564-569
  unsaturated, detection, 558
Ointments, sterilization, 727
Oiticica oil, 574
"Old tuberculin," 690
Olefines, 422, 425, 457, 531, 533
Oleic acid, 553, 554, 557, 559, 565, 567, 570, 791
Olive oil, 555-559, 727, 789
Onion root tips, rays from, 767
Oöcysts, *Eimeria tenella*, lethal action on, 717
Opsonic index, 775
Opsonins, 757, 759
Optical activity, and photochemistry, 266-268
Optimum wave-length for lethal action, 701, 706, 714
Oranges, killing molds on, 711
Orange II, 625, 532
Orbital quantum numbers, 226
Orbits, electronic in atoms, 21-23
Orders of spectra, 33
Organic acids, 184, 186, 361, 362, 540
  dyes, detection, 575
Organizer, embryonic, 765
Organometallic compounds, 464, 465
Ortho hydrogen, 226
Ortho-para hydrogen conversion, 244
Orthostannic acid, 366
Oscillator, molecular, 220, 223, 224, 232-235
Oscillatory circuit, for starting mercury arc, 92
Oscillograph, cathode-ray, 271
Osmundia claytoniana, 890
Osram lamp, 68, 175, 539, 640
Ostwald color system, 581
Ova, roundworm, 718
Overall photochemical reactions, 245-256
Ovoflavin, 852
Ovoverdin, 859
Oxalates, 267, 441-445
Oxalic acid, 205, 469, 503
  absorption spectrum, 441
  actinometer, 202
Oxalic acid, and aniline, 495
  and ferric salts, 361
  and pinene, 515
  bromine reaction, 447
  chlorination, 541
  effect on manganioxalate photolysis, 442
  formation, 405, 451, 467, 470, 480, 484, 514, 869
  in photosynthesis, 867
  in tobacco plant, 884
  iodine reaction, after-effect, 447
  oxidation, 251, 252, 350, 366, 441, 443, 448
  photolysis, 103-105, 246, 440, 441, 443-447
  reaction with hydrogen iodide, 249
Oxalyl chloride, 448
Oxanthrol, 508
Oxanthrone, 508
Oxazine dyes, 640
Oxen, light sensitization, 861
Oxidase, 671, 742, 749, 756
Oximes, 410, 493, 494
4-Oxo-9,10,11,12,13,14-octadecatrienylcarboxylic acid, 574
Oxyacetylene flame, 35
Oxycellulose, 614, 615, 617, 618
Oxygen, 192, 279, 345, 348, 359, 370, 407, 457, 467, 468, 471, 479, 649
  absorption spectrum, 179, 181, 193, 194, 249, 293-295
  active, 292, 349, 468, 727, 728, 864
  and biological photosensitization, 862, 863, 864
  and chlorophyll, 871, 872, 877
  and fluorescence quenching, 262-264, 864
  and plant photosynthesis, 876-880
  and polymerizations, 410, 489, 584, 595
  and rubber, 595, 596, 601
  and textiles, 615, 621, 626
  and vitamin D production 797, 798, 804, 806, 807
  as free radical, 295
  atomic, 251, 252, 304, 475
    excited, 293, 296, 297, 300, 309
    reactions, 300, 302, 309
  combination with nitrogen, 324
  dissociation, 293, 294, 300, 309
  effect on acetone fluorescence, 426
  effect on photohalogenations, 529, 532-535, 537, 540-542, 545, 546
  effect on hydrogen-chlorine combination, 281, 283, 285, 287-289, 302
  effect on nitrogen peroxide fluorescence, 327
  effect on oxidation of lactic acid, 448
  effects on various photolyses, 296, 297, 315, 327-330, 332, 367, 377, 397, 400, 417, 442, 444, 460, 462, 515, 853
  electrical conductivity, 473, 514
  equilibrium between O_2 and O_4, 294, 295
  evolution from photoöxides, 508-511
  excitation, 243
  excited molecules, 294, 295, 300
  filter, 309
  formation, 64, 305-307, 346-348, 352, 475
  heat of dissociation, 235, 243, 293, 294, 354
  in accelerated paint tests, 578, 579
  in gasoline testing, 653-655
  in milk irradiation, 840, 841
  in plant cells, 874
  inhibitor of phosgene formation, 311-314
  ion, 264
  isotopes, 227
  liberation by plants, 866
  magnetic susceptibility, 294, 295
  metastable, 264
  migration from nitro group, 516
  predissociation, 293, 300
  purification, 510
  transformation to ozone, 292-295
Oxygenase, 889
Oxyhemoglobin, 750
Oxyhydrogen flame, 35
"Oxyn" acids, 564
2-Oxyquinoxaline-3-aldehyde, 851
Oxytocic hormone, pituitary, 689
Ozone, 345, 350, 401, 411, 413, 556, 568, 625, 650, 727, 733, 788

Ozone, absorption of ultraviolet rays, 7, 193, 194, 295-297
and dyes, 633, 634, 638, 640
and hydrogen peroxide, 339
and insulin, 679
and isoeugenol, 514
and paper, 619
and pyridine, 519
and rubber, 597, 598, 602, 603, 606
and vitamins, 804, 840, 848
bleaching by, 618
excited molecules, 296
formation, 292-295, 299-300, 309
in accelerated paint tests, 579
in atmosphere, 193
in food irradiation, 828, 829
in laundries, 727
in vitamin D production, 832
inhibitor of Eder reaction, 445
photolysis, 211, 259, 292, 295-298
toxicity, 293
Ozonides, 410, 415, 728

P branch, 223, 225
Paintings, fluorescence, 663
Paints, accelerated tests, 575-581
bleaching, 575, 576
chlorinated rubber, 611
drying tests, 574
films, 572, 577-579
for rubber, 610
luminous, 583
outdoor exposure tests, 578, 581
reflecting properties, 583
stable to ultraviolet rays, 183
ultraviolet-reflecting, 583
Palatinol, 589
Palisade cells, in irradiated plants, 715
Palladium, 159, 161
Palm oil, 556, 610
pitch, in ebonite, 608
Palmitates, 586
Pancreas, secretory activity, 760
Pancreatic diastase, 681
Pancreatin, 681, 682
Papaveraldine, 520, 521
Papaverine, 520, 521
Paper, 561, 619, 625, 644
bleaching, 617, 618, 644
deterioration, 618-620
dyed, 643, 644
fluorescence tests, 620, 644, 663
light-sensitive, 363, 384
pH, 644
photographic, 363, 383, 384, 647, 648
pulp, yellowing, 618
rolls, removing electric charges from, 662
testing, 641
ultraviolet penetration, 619
ultraviolet reflection, 618, 619
water resistance, 620
yellowing, 562
Papillomas, 766
Paracetaldehyde, 422
Paraldehyde, 418, 613
Paracyanogen, 456
Paraffin oil, 508
Paraffins, 531, 533, 607, 610, 651-653, 661
Paraformaldehyde, 460
Para hydrogen, 226, 274, 290, 317, 397, 402, 420, 439, 811
Paramagnetic ions, and fluorescence quenching, 263
Paramecia, lethal action on, 523, 696, 700, 701, 703, 716, 717, 752, 860, 865
Paraquinone, and rubber oxidation, 603
Parathyroids, 755, 790, 819
Parathyroidectomy, 749, 755
Paratoluidine, reaction with crotonic acid, 456
Para toners, 590
Parazone, 604
Parchment, 561, 562
Particles, in atmosphere, 194
Pasadena, solar energy at, 199
Paschen series, 20, 22, 163
Pasteurella infection, 776
Patent leather, 293, 572, 650
Pauli exclusion principle, 25
Pauly test, wool, 623
Peaches, composition, 891
Peanut oil, 559, 743, 790, 795, 828
Pears, composition, 891
Peas, 886, 889
Pelargonic acid, 559
Pelargonium leaves, 715, 872, 873
Pellagra-preventing factor, photolysis, 850
Pentachlorobenzene, 543
Pentachlorocyclohexane carboxylic acid, 547
Pentachloroethane, 401, 535
Pentacyanoaquoferrate, 362, 363
Pentacyanoaquoferrite, 362
Pentadiene, tetraphenyl, 411
Pentahydroxyamylbenzimidazole, 851
Pentane, 394, 526, 527, 529, 531
Pentathionic acid, 354, 390
Pentene, isomerization, 413
Pentosans, 883
Pentoses, 435
Pentyl chloride, 531
Pentylene, 394
Peppermint oil, 513
Pepsin, 247, 680, 683, 890
Peptides, 676, 677
Peptones, 411, 674
Peracetic acid, 422, 484
Peracid, furo, 517
Peracids, 422, 880
Peraldehyde, 880
Perbenzoic acid, 473
Perborates, 410, 657
Percarbonates, 410, 657
Perchlorates, 298, 307, 341, 346, 348, 349, 455
Perchloroethylene, 657
Performic acid, 440
Perfructose, 433
Perichecia, of fungi, 890
Perilla oil, 567, 571, 573, 574
Periodates, 348
Periodic reactions, 256
Permanent Red 4B, lake, 643
Permeability, of erythrocytes, 750, 752
of membranes and irradiation, 669
Peroxidase, 685, 686, 742, 889
Peroxides, 433, 440, 473, 481, 561
and oleic acid, 553
and polymerizations, 584
and vitamin D, 804
formation, 403, 422, 467, 468, 653, 654, 656, 812
in alcohol irradiation, 402, 404
in ether, 405
in irradiated oils, 727, 728
in photodynamic action, 863
in plant photosynthesis, 876, 881
in rubber oxidation, 604
mono and di-alkyl, 339
of dyes, 633
of fats and oils, 558-560, 572
of linoleic acid, 553
of porphyrin, 680
of rubrene derivatives, 509-511
organic, 383, 407, 411
Per salts, 411
Perseulose, 432
Persulfate ion, 355
Perylene, 512, 595
"Peter Pan" gingham, 642
Petrolatum, 652, 727
Petroleum products, 530, 531, 651-657
Phenanthrene, 504, 508, 511, 550, 591
Phenanthrenequinone, 482, 603
Phenazines, 497, 498, 522
Phenetidine, 497
Phenols, 356, 390, 469, 479, 499, 500, 562, 573, 631, 648, 657, 833
acyl derivatives, 647, 648
amino, 468, 496, 497
and aldehydes, 584
and chlorophyll bleaching, 871
and insulin, 679

Phenols, and nitrocellulose, 463
and rubber oxidation, 603
as fluorescence quenchers, 262
chloronitroso, 479
dinitro, 499
fluorescence, 600
galactoside, 680
glucoside, 680
homologs, esters, 547
inhibitors, 340, 410, 445, 474
oxidation, 863
mannoside, 680
nitro, 499
resins, 410, 584, 585, 592, 611
vinyl derivatives, 411
Phenolase, 742
Phenolphthalein, 259, 629
Phenosafranine, 260, 264, 498, 631
Phenoxybenzoylacrylic acid, 491
Phenylacetaldehyde, 424, 473
Phenylacetic acid, 477, 478
Phenylacetylene, iodination, 538
Phenylacridine, 509
Phenylalanine, 670, 671, 696, 739
Phenylanthracene, 508, 509
Phenylazobenzene, 575
Phenyl benzoate, 480
4-Phenylbenzohydrol, 477
4-Phenylbenzophenone, 477
Phenyl bromide, 544
2-Phenyl-1,3-butadiene sulfone, 413
9-Phenyl-10-carboxyanthracene, 508
Phenyl chloride, 543
Phenylcinnamic acid, bromination, 487
Phenylcinnamonitrile, 485, 488, 743
Phenylcinnamylideneacetonitrile, 484
Phenyldiazonium chlorides, 500
Phenyldibenzoxanthrenium dyes, 647
Phenylenediamine, 260, 495, 498, 575, 646
Phenylethyl chloride, 546
Phenylethylene, 488
Phenylethylindane, 811
Phenylfluorenes, 512
Phenylfluorenylcarbinols, 512
Phenyl fluoride, 544
Phenylglyoxal osazone, 450
Phenylglyoxime, 461
Phenylheptatrienic acid, 492
Phenylhydrazine, 183, 450, 478, 498, 575, 614, 625, 626, 630
Phenylhydroxylamine, 470, 496
Phenylhydroxystyryl ketones, 493
Phenylindole, 743
9-Phenyl-10-iodoanthracene, 508
Phenyl iodide, 644
Phenylmethyl carbinol, 403
Phenyllactic acid, 540
3-Phenyl-2-methylindone, 492
Phenylmethyl ketone, 595
2-Phenyl-6-methylquinoline, 521
Phenylmorpholines, 612
Phenyl-α-naphthylamine, 604
Phenyl-α-naphthyl ketone, 477
Phenyl-β-phenylstyryl ketone, semicarbazone, 494
β-Phenyl-β′-phenyltruxone, 517
Phenylpropiolic acid, 541
Phenylpyrazolines, 478
Phenylquinoline, 743
Phenylquinoline carboxylic acids, 521
Phenyl radical, 472
Phenylsemicarbazone, 495
2-Phenyl-5-styryl-6-nitroisatogen, 471
Phenylurethane, 875, 877
Phenylvinylacetic acid, 413
Pheophorbide-*b*, fluorescence, 879
Pheophytin, 764
Phloroglucinol, 479, 630, 648
Phloxin, 264
Phosgene, 227, 311
decomposition, 314-317
formation, 310-314, 346, 394, 400, 448, 460, 532-535
Phosphatase, 683, 754, 785, 818, 819, 822
Phosphate glass, 132, 133, 172, 176
Phosphates, 681, 784, 785, 818, 828
Phosphatides, 670, 791
Phosphine, 332, 333, 359
Phosphite, 370
Phosphorescence, 262, 264, 265, 375, 385, 665
Phosphoric acid, 369, 669, 710, 753
Phosphorus, 64, 141, 358, 596, 778
absorption, 745
and rickets, 779, 783-786, 818, 820, 830
chlorides, 64, 545
conversion of yellow to red, 359, 596, 598
in blood, 774, 778, 783-785, 788, 822
in plants, 888, 889
nitride, 218, 219
pentoxide, 168, 179
red, 332, 540
Photoanisotropy, 266, 283
induced, 383
Photocellulose, 614
Photochemical processes, theories of mechanism, 205-216
Photochemistry, early work, 205
Photocolorimeter, 636
Photoconductivity, 269, 380
Photodichroism, 266, 857
Photodynamic actions, 260, 261, 860, 861, 865
Photoelectric cells, 97, 99, 100, 107, 271, 771
effect, 17, 214, 269, 375, 505, 732, 733, 877
Photoelectrons, liberated by x-rays, 209
Photoequivalence law, 207, 210-213
Photofluorescein, 864, 865
Photographic desensitizers, 863
papers, 255, 647, 648
plates, 180, 209, 271
processes, non-silver, 365, 384, 481, 485
Photography, chromated gelatin, 365
Photoionization, 269
Photoisopyrocalciferol, 810
Photometers, 105, 107, 161, 270
Photon, 10, 18
Photonitrification, 351
Photooxides, of hydrocarbons, 508-510
Photoprocesses, in crystals, 372-376
in liquid and gas phases compared, 335, 336
Photopyridine, 433, 519, 520, 646
Photopyrocalciferol, 810
Photosphere, 191
Photronic cells, 96, 97
Photosantonic acid, 516
Photosensitizations, 257-269, 336, 380, 381, 510, 741, 745, 860, 862-864
Photosensitizers, 257, 862
Photostationary states, 274, 504
Photosynthesis of carbohydrates, 873-882
Photosynthetic units, 881
Phototropy, 371
Phototropy, 268, 481, 489, 493-495, 516, 521
Photovoltaic effects, 269, 464
Phthalanil, 592
Phthaldehydic acid, 548
Phthalein dyes, 629
Phthalic acid, 469, 481, 507, 617
Phthalic anhydride, 617
Phthalic esters of hydroquinone ethers, 591
Phthalide, 548
Phthalimide, 550, 592
Phthiocol, 502
Phycoerythrin, 881
Phylloporphyrin, 861
Phylloerythrin, 872
Phytin, and fermentation, 710
Phytoplankton, 790
Phytosterol, 791, 872
Picea excelsa, 873
Picein, 162, 436
Pickering lines, 33
Picoline, 518
Picolinic acid, 518, 520
Picramic acid, 498
Picric acid, 101, 354, 472, 498, 499, 598
Pigmentation of fruits, 890, 891
of human skin, 734, 739, 740, 772, 773
Pigments, 575, 581-583, 589, 590, 608, 609
fading, 205
formation in bacteria, 888
fluorescence analysis, 575

Pigments, on mustard, 886
Pigs, 746, 786
Pilchard oil, 574
Pilocarpine, 522
Pimpinellin, 515
Pinachrome, 632
Pinacolone, 538, 539
Pinacols, 477, 514, 517, 816
Pinacone, 404
Pinacryptol, 264, 265, 498, 863
Pinacyanol, 334, 381, 465
Pinaverdol, 632, 871
Pine bark extract, 167, 563
  oil, 610, 657, 659
  pitch, 610
Pinenes, 210, 473, 514, 515
Pinus strobus, 873
Piperidine derivatives, 425, 466, 525, 598
Piperitone, 515
von Pirquet test, 775
Pisum, seedlings, 888
Pitch, 662
Pittsburgh, solar radiation at, 201
Pituitary, oxytocic hormone, 689
Pityriasis rosea, 769
Placental hormones, 689
Planck's constant, 8, 10, 18, 207
Plants, ash, 889
  coumarin formation, 487
  development, 58, 150, 205, 886-888
  diseases, 890
  lethal action on, 715, 886
  oils, activated, 815
  respiration, 889
Plasteins, 674
Plaster of Paris, 768
Plastics, 410, 411
Plasticizers, 173, 409, 589, 590, 612, 650
Platinic acid, 248, 369, 370
Platinum, 74, 131, 253, 339, 364, 369, 415
  catalyst, 341, 439, 454
  sol, 386, 388, 390
"Plexiglas," 172
Plums, composition, 891
Pneumococcus, 776, 824
Polarized light, 266-268, 348, 353, 368, 383, 698, 882
Pole-caps, for therapy lamp, 133, 134
Pole-vessels, mercury arc, 79
"Pollopas," 165
Polyatomic molecules, 223, 224, 236, 240, 241, 244
Polycarboxylic acids, 481
Polychlorohydrocarbons, 531
Polychromatic light, photoreactions by, 254, 255
Polyglycolide, 451
Polymerization, 406, 408-411, 557, 564-567
Polymers, benzaldehyde, 511
  bivinyl, 411
  from isopropenylmethyl ketone, 429
  of acrylic esters, 584
  vinyl esters, 410
Polyneuritis, 851
Polyphenols, antioxidants, 610
Polysaccharides, 869
Polystyrenes, 488
Polyvinyl chloride, 411
Ponceau R G, 636, 637, 640, 642
Pongee, 188
Poppyseed oil, 571, 572, 574
Pork production, and sunlight, 785
Porphyrins, 261, 263, 553, 685, 687, 751, 767, 860, 861
Porphyrinuria, 861
Porphyropsin, 859
Positive branch, 223
Potash, 166, 171
Potassium acetate, 183
  acid phthalate, 185
  alum, 612
  amalgam, 360
  amide, 349, 350
  and muscle, 760
  anthraquinone sulfonates, 506
  antimonyl tartrate, 450
  arsenic tartrate, 450
Potassium bichromate, 620
  bismuth tartrate, 450
  bisulfate, 357
  borotartrate, 450
  bromide, 383, 433, 434, 450, 538, 540, 681
  carbonate, 176, 869
  chlorate, 348, 495
  chloride, 141, 183, 383, 434, 681, 704
  chromate, 179, 187, 364, 522
  cobalticyanide, 363
  cobaltioxalate, 441, 442
  copper tartrate, 450
  cuprioxalate, 442
  cyanide, 265, 363, 439, 480, 627, 629, 812, 863
  dichromate, 187, 336, 344, 364, 365, 404, 439, 469, 612, 629, 646
  ferricyanide, 363, 495, 646
  ferrioxalate, 442, 443
  ferrocyanide, 362, 363, 405, 631
  fluoride, 141, 440
  formate, 344, 345
  hydrogen phthalate, 187
  hydrogen phosphate, 684
  hydroxide, 185, 358, 362, 508
  iodate, 345
  iodide, 187, 433, 434, 446, 541, 629, 680, 685
    and metabolism, 745, 759
    crystals, 372, 373
    oxidation, 251, 260, 343, 344, 348, 371, 384
    photolysis, 104, 247, 342, 343, 370
  in blood, 754
  ion, 682, 761
  iron tartrate, 450
  manganioxalate, 267, 442
  mercuric oxalate, 444
  nitrate, 102, 104, 176, 498, 681, 800, 883
    photolysis, 348, 352, 353
  nitrite, 255, 351, 352, 882
  of skin, 742
  oleate, 553
  oxide, 168
  oxalate, 254, 344, 345, 442, 445-447
  palmitate, 553
  permanganate, 252, 364, 371, 452, 614
  persulfate, 209, 251, 357, 358, 371
  sulfate, 358, 390
  stearate, 553
  tellurate, 384
  thiocyanate, 358, 675
Potato chips, rancidity, 561
  tubers, solanine content, 890
Potential energy curves, 163, 229, 232-236, 239, 241, 242, 374, 375, 453
Potentials, ionization, 27
  oxidation-reduction, 433
  resonance, 27
  sparking, 40
Poultry (see Chicks)
Powders, gun, 462
Precipitins, 759
Predissociation, 214, 235, 241-244, 263
Preen glands, 787
Preserves, sterilization, 722
Primary process, photochemical, 207, 211-214, 216, 227, 229-245, 336
Principal series, 23, 24
Prints, 479, 622
Prism, 4, 6, 190
Probes, 31, 48
Prolan, 689
Proline, 676, 703
Propanes, 258, 394, 396, 429, 526, 531, 532, 546, 550, 612
  chlorinated, 532, 534
Propanol, 404, 538
Propene, 429
Propenylmethyl ketone, 429
Propionaldehyde, 244, 397, 404, 416, 421, 425
  hexahydrophenyl, 424, 473
Propionanilide, 438
Propionic acid, 404, 437, 438, 441, 540
Propiolic acid, phenyl, 541
Propiophenone sulfonic acid, 413
Propyl alcohol (see Propanol)
  bromide, isomerization, 399

Propyl ethylene, 429
  disulfide, and gasoline, 654
  iodide, photolysis, 396, 398
  radical, 429
Propylene, 396, 407, 422, 534
Provitamin D, 792
Prussian blue, 341, 362-364, 390
Protective glasses, 164-167
  wrappers for foods, 560-563
"Protectoid," 165
Proteinases, 683, 684
Proteins, 181, 411, 674-680, 696, 701, 705, 716, 717, 739, 740, 873
  blood, 756, 863
  denaturation, 365, 675, 676
  disintegrated, 753, 773
  fluorescence, 735
  in antibodies, 758, 759
  irradiated and gold sols, 669
  light absorption, 670
  metabolism, 745
  of lens, 763
  of lymph, 751
  of retina, 858
  oxidation, 671, 863
  photosynthesis, 882, 883, 887
  protective action on pepsin, 684
  reaction in surfaces, 265
  shock, 734, 773
Proteose, 677
Prothrombin, 684
Protochlorophyll, 888
Protoplasm, 767
Protozoa, lethal action on, 247, 701, 716, 717
Pseudobutylene, 407, 408
Pseudocumene, 469, 550
Pseudocumidine, 647
Pseudoglobulin, 677
Pseudonitric acid, 352
Psoriasis, 769
Pteris longifolia, 890
Puccinia spores, 711
Pulfrich step photometer, 581, 636
Pulmonaria leaves, 715
Pulp, wood, 618, 645
Pump, Gaede, 148
Punicic acid. 566
Purines, 698, 700, 701, 703, 746, 850, 851, 863
Purple bacteria, photosynthesis by, 881
Pustular folliculitis, 769
Pyocyanine, 522
Pyran derivative, 268
Pyrazole, formation, 460
  Yellow, 632
Pyrazolines, 1-phenyl, 478
Pyrazolone dyes, 640
Pyrene compounds, 183, 562
Pyrethrum, toxicity, 658, 659
Pyrex, 72, 75, 103, 146
Pyridine and derivatives, 356, 407, 433, 518-521, 613, 687, 703
Pyridinium bromide, hexadecyl, 644
Pyridinium 1-nitronaphthalene-8-sulfonate, 502
Pyridones, *N*-methyl, 261
Pyridoxine, 850
Pyrimidines, 698-703, 850, 851
Pyrocalciferol, 807, 810-812
Pyrocatechol, 469, 509
Pyrogallol, 260, 410, 475, 631, 688
Pyroxylin, 562, 591
Pyrrole, derivatives, 466, 518
Pyrrolidines, formation, 407
Pyruvic acid, 421, 449, 451, 518, 630, 702
Pyruvic dehydrogenase, 687

Q branch, 223, 225
Quanta, for carbohydrate photosynthesis, 866
  required to kill a bacterium, 705, 706
  values at various wave-lengths, 207
Quantum, of action, 8
  mechanics, 25, 26, 217, 236, 372, 374, 375, 453
  numbers, 21-25, 220-223, 226
  theory, 10, 11, 17, 18, 21, 22, 206, 218-226
Quantum yield, 102, 104, 105, 210-213, 247, 248, 251, 252, 336, 373
  fumaric-maleic interconversions, 453, 454
  hydrogen-chlorine combination, 289-291
  hydrogen iodide photolysis, 272
  in plant photosynthesis, 874-876, 879-881
  in lethal irradiations, 705
  milk irradiation, 844
  ozone photolysis, 296, 297
Quartz, 7, 74, 151, 165, 169, 172-175
"Quartzlite," 170, 173-175, 181, 185
Quebracho extract, 563
Quercitin, 621
Quinaldine, 522, 592
Quinic acid, monoacyl derivatives, 523
Quinidine sulfate, 523
Quinine, 206, 210, 340, 523-525, 658, 664
  bichloride, 522
  bisulfate, 441, 522, 743
  sulfate, 183, 252, 347, 356, 500, 523, 562, 640, 657
Quininic acid, 521
Quinol, 469, 726
Quinoline derivatives, 521, 743
  dyes, 640
Quinones, 101, 474, 479-481, 507, 596, 622, 679, 871
Quinotoxin, 523
Quinoxaline, 851
Quinoneoximes, 471

R branch, 223, 225
Rabbits, oxygen consumption, 744
Racemization, 512
Radiation, continuous for absorption measurements, 152-163
  emission mechanism, 11, 15-29
  erythema-producing, 100, 101
  infrared, 2, 6
  lethal, 100, 101, 143, 193
  measurement of, 96, 97, 100
  mitogenetic, 101, 150, 767, 768
  necrobiotic, 768
  processes, stellar, 191, 192
  resonance, 190
  solar, ultraviolet in, 1, 2, 142, 191
  synergy of wave-lengths, 442, 443, 486
  tan-producing, 57
  theory of reactions, 209, 210
  ultraviolet, nature of, 2, 6, 7
  visible, nature of, 2, 3, 4, 6
Radiationless transitions, 242
Radicals, free, 231, 244, 864
Radioactive emanations, and petroleum products, 655
Radiomalt, 832
Radiotoxic spectral sensitivity, 714
  thresholds, 714
  virulence, 714
Radium, 467, 683, 686, 733
Raffinose, 435, 890
Rag papers, 620, 644
Raman effect, filters for, 188
  source for, 137, 138, 149
  spectra, 213, 222, 224, 593, 665
  of gasolines, 665
  of rubber, 593
Rana pipiens, 766
Rancidity, 558, 559, 560, 562, 563
Rapid Filter Yellow, 632
Rare earths, 19, 166, 261, 369, 370
Rates, photochemical reaction, 207, 245, 246, 251-253
Rayons, 188, 613, 619-621
Rays (see Radiations)
Reactance, in starting mercury arc, 76
Reactions, chain, 213-215
  overall photochemical, 245-256
Realgar, 359
Reciprocity law, 101, 271
Recombination, of atoms, 231, 253, 279, 280, 335
Rectifier, for starting a.c. mercury arc, 92
Red algae, photosynthesis, 881
Red blood cells (see Erythrocytes).

Red lead, 577, 583
Red oil, 557
Reduced mass, 236
Reduction potentials, of dyes, 531
Reflectance, of skin, 738
Reflectors, 771, 844
Refraction, 4
Regenerated cellulose, 184, 619
Reichert-Meissl number, 837
Reindel's isoergosterol, 796, 797
Rennet, 247, 684
Rennin, 658
Rentschler meter, 201, 202
Resins, 410, 411, 584, 585, 589, 592, 610, 619, 655, 663
Resinate, 585, 612
Resonance, 262, 263
lines, 37, 92, 117-119, 121, 124, 127, 136, 137, 141, 150, 151, 190, 257
potentials, 8, 26, 27
Resorcinol, 469, 630, 688
Resorcinolazobenzene, 562
Respiration, 687, 863, 867, 874, 877, 889
of plants, 889
Respiratory center, 753
enzymes, 687, 688, 891
quotient, 746
Reticulocytes, 748, 749
Retina, 164, 687, 733, 762, 857, 858
Retinene, 858
Reversed lines, underwater spark, 152
Reversing layer, sun, 192
Revertex, 611
Rhamnose, 432, 472
Rhinitis, 776
Rhodamine, 142, 188, 260, 383, 451, 585, 620, 634, 639
Rhodium, 74
Rhodovibrio, 707
Ribbons, sterilization, 727
Rice, 685
Ricin, 690
Ricinoleic acid, 554
Ricinus communis seeds, 683
Rickets, 143, 174, 733, 738, 778, 779, 781-785, 827, 862
Ringer's solution, irradiated, 761
Road tar, accelerated weathering test, 661
Rochelle salt, reaction with bromine, 252
Rock salt, 372, 373
Rods, of retina, 857
Root storage, 887
Rose Bengal, 264, 634, 863
Rosin, 557, 585, 586, 610, 619, 620, 644
Rosindulin, leucobase, 678
Rosindulines, formation, 517
Rotational energy levels, 218, 220, 222, 229
Rotenone, 659
Rubber, accelerated weathering tests, 562, 605-609
bonding, 611
cements, gelatin, 597
chlorinated, 611, 612
composition soles, 608
curing, 598
fluorescence, 601
oxidation, 601-605
plants, 890
polymerization, 429, 593-597, 601, 602
preservation, 609, 610
Raman spectrum, 593
reclaimed, 607
sols, 593-595
stretched, X-ray diagram, 593
substitutes, 411, 558, 573, 612
surface films, 599
synthetic, 593
Rubberseed oil, 574
Rubene, tetraphenyl, 509
Rubidium, 238
Rubidium iodide, 238
Rubrene derivatives, 509-511, 603, 864
Ruhmkorff coil, 76
Russell effect, 383, 556, 790
Ruthenium hydroxide, 370
pentacarbonyl, 370
Rydberg constant, 32
formula, 20, 22, 23
Rye, germinating, 885

Saccharomyces, (see Yeast)
Safe-T-Aire equipment, 729
Safety glass, 411, 588, 591
Safranine, 260, 585, 630, 634, 639
St. John's wort, 861
Salicin, 436
Salicylaldehyde, 423, 476, 481
Salicylates, ultraviolet sensitizer for plates, 381, 382
Salicylic acid, 478, 481, 548, 725, 741
Salivary diastase, 681, 682
Salkowsky reaction, 623
Salmo lacustris, embryos, 765
Sal. typhimurium, 706
Salol, 562
Salvia plants, minerals in, 889
"Sanalux," 173
Sanocrysin, 744
Santonin, 516
Saponin, 382, 436, 824
Sarcoma, 766, 828
Sassafras oil, 513
Sawdust, irradiated, 788
Scandium lines, 26
Scarlet HR, 647
Scatole, 517
Schenectady, solar energy at, 197, 198
Schüler cathodes, 151
Schütz law, 681
Schumann plates, 7, 381
region, 7, 8, 208, 231, 241, 293, 300
-Runge bands, 293-295
Schwarzschild law, 271
Scleroderma, 742
Sclerotium batacicola, 711
Scrofuloderma, 769
Scurvy, 849
Sea urchin eggs, 764
Secondary photochemical processes, 211, 212, 214, 216, 245, 248, 250, 253, 254, 335
Secretin, 689
Sector, rotating, 254, 270, 446, 447, 486, 875
Sedimentation, red blood cells, 756
Seedlings, 715, 885, 886
Seeds, 887, 890
Selection principles, 24, 25, 220, 222, 225, 226, 243
Selective irradiation, 726, 828
Selenides, 142
Selenious acid, 384, 514
Selenium, 148, 269, 358, 384
chlorides, 545
oxides, 360, 431
red, 598, 599
Selenomercaptan, and gum formation in gasolines, 656
Self-extinction, 262
Self-inductance coil, 41, 42
Self-reversal, 65
of mercury lines, 65, 109, 110
Semiacetals, 437
Semicarbazones, 490, 491, 494, 495
Semi-ebonites, fluorescence, 601
Semiquinones, 263
Sensitivity, photographic, theories, 378, 379
Sensitization (see Photosensitization)
Separation of lines by refraction, 189, 190
Sericin, 622
Series, spectral, 23, 24, 163
Serine, 672
Serum albumin, 674-678, 862
amylase, 756
and pancreatin, 682
antitryptic activity, 757
calcium, 754, 784 (see also Calcium, in blood)
cholesterol, 755, 825
globulin, 675-677, 706
index of refraction, 756
inorganic phosphorus, 710, 754
irradiated, 674, 675, 677, 706, 751, 753, 756, 758, 863

Serum albumin, "kalicrein," 691
opsonins, 757
protective action on venom, 691
reducing power, 710
surface tension, 756
vasoconstricting power, 746, 747
Sesame oil, 559
Shale oil, 865
Shark-liver oil, 855
Sharp series, 23, 24
Shaving creams, sterilization, 727
Sheep, 861
Shellac, white, 382
Shock, 733
Siak-illipe nut, sterols, 792
Silane, 333
Silent discharge, 292, 310
Silica, 165, 166, 168-172, 179, 189, 583
gel, 264, 391, 392
Silicates, in carbon arc, 58
Silicon carbide, 51
oxychloride, 288, 289
tetrachloride, 64
tetrafluoride, 51
Silk, 188, 613, 620-622, 642, 674
artificial, 188, 613, 616, 620, 621
dye-fading, 502, 622, 637, 639
Silkworm eggs, catalase, 685
Siloxene, 333
Silver, 97, 150, 231, 378, 380, 398, 415, 463
acetate, 438
acetylide-gelatin emulsion, 384
azide-gelatin emulsion, 384
bromide, 240, 373, 376-378, 380, 381, 599
chloride, 6, 240, 349, 376, 377, 383
chromate-gelatin gels, 391
filters, 150, 178, 762
halides, 237, 240, 376-380, 383
iodide, 239, 240, 376, 378
nitrate, 260, 364, 439, 726
and cholesterol, 812
gelatin gels, 391
preparation of silver sols, 387
reaction with zinc oxide, 371
reduction, 159, 383, 384
oxalate, 384, 441
oxides, 371, 410, 508
salts, 205, 359, 371, 384, 645
sols, 386-390
sulfide, 379
thioarsenite, 389
Sinapis alba, nitrogen content, 884
Sipalin, 576, 650
Sitosterols, 792
7-dehydro, 811, 816, 817
Sizes, for cloth or paper, 411
Skin, 669, 678, 684, 713, 733-744
absorption of vitamin D, 847
active oxygen in, 727
and parathyroids, 755
and typhoid immunization, 757
cholesterol, 766, 791
cream, irradiated, 847
fluorescence, 651
glutathione, 751
grafting, 770
infections, 774, 775
lipase, 756
proteinase, 756
provitamin, 795, 814, 816
respiration, 826
senile, 769
substance affecting castrated mice, 756
sugar, 751
tumors, and irradiation, 511, 742, 766, 865
vitamin C content, 849
wounds, 825
Sky Blue, 639
Skyshine, 198-202, 782, 828
Smoke, in air, 196, 201, 202
Smokeless powders, 462
Snail lipins, 792
Snake venom, 691
Soaps, 555, 556, 563, 582, 648, 741, 847
Sockets, after tooth extraction, 769
Soda, 171
Sodium, 27, 131, 141, 231, 238, 257, 360, 373, 674
acetate, 183, 434, 437
alcoholate, 476
alizarine sulfonate, 646
amide, 349, 350
anthraquinone sulfonates, 449, 506, 682
azide, 354, 363, 481
benzoate, 185
3-benzoyl-aminopyrenedisulfonate, 562
bicarbonate, 354, 450
bromide, 567
carbonate, 450
chlorate, 347, 646
chloride, 183, 373, 375, 433, 675, 681, 704, 763
chlorite, 347
2-chloroanthraquinone-6-sulfonate, 506
chlorocinnamate, 483
N-chloro-p-toluenesulfonamide, 265
cinnamate, 187
cholate, 670
chromate, 364
cyanide, 354, 749, 750
dichloroanthracenedisulfonate, 682
dichromate, 407, 408, 502, 616
fluorescein, 864
fluoride, 172, 681
formate, reaction with iodine, 252, 440
fumarate, 452
glycocholate, 670
glycol, 411
hydrosulfite, 358, 463, 507
hydroxide, 187, 450, 508
hypochlorite, 346, 347, 589
hypophosphite, 370
hyposulfite, 616
iodide, 231, 237, 238, 342, 344, 372, 373
ketyl radical, 477
lactate, 449
maleate, 452
molybdate, 369, 383, 619
naphthionate, 503, 631
nitrate, 440, 498, 646, 681, 883
nitrite, 249, 344, 345, 351, 371, 377, 439
nitroferrocyanide, 363
nitroprusside, 341, 363, 364
nucleate, 703
peroxide, 573
6-phenyl-2-aminopseudoaziminobenzenedisulfonate, 648
phenylbenzimidazolesulfonate, 743
phenyldiazosulfonate, 645
7-phenylheptatrienic acid, 492
phosphates, 172, 370, 640
pyrenetetrasulfonate, 562
oleate, 391, 555
oxide, 168, 179
resinate, 619
salicylate, 481
selenite, 817
silicate, 763
stannate, 619
sulfate, 340, 341, 691
sulfide, 495
sulfite, 356, 357, 410, 450, 863
tartrate, 450
thiocyanate, 358
thiosulfate, 358, 598
toluenesulfonchloroamide, 498
triiodomethanesulfonate, 400
tungstate, 383, 387
"Soft-lite," 166
Soil, 350, 351, 391
Solanine, formation in potatoes, 890
Solar constant, 1, 2
energy distribution, 7, 142, 191, 192, 195-202
oil, 531, 653
Solarium arcs, 62, 63
Solarization, 173-176
Solio paper, 640
Sollux lamp, 580
Sol-rubber, 593, 594
Solvates, 437
Solvation, 249, 335-337

Sorbitol, 433, 472
Sorbose, 432, 867
Sound records, 662
Sources, continuous for absorption studies, 152-163
dual purpose, 142-147
illuminating, 15
of radiations, survey, 30-37
standardization by oxalic acid photolysis, 443
Soybean oil, 557, 559, 567, 573, 574
Soybeans, 830
Soy urease, 684
Spark, aluminum, 38, 44
as ultraviolet source, 38-45
cadmium, 155
carbon, 154
cobalt, 44
condensed, 42
discharge, theory, 39-42
gaps, 43, 44
iron, 38, 152
irradiated, 269
lead, 155
magnesium, 155
molybdenum, 154
nickel, 154
reactions induced by, 45
sources for photochemical reactions, 43-45
spectra, 32, 33, 36, 42
Tesla, 155
tin, 155
tungsten, 152, 154, 155
uncondensed, 40
underwater, 152, 153, 155
uses, 38-45, 650
zinc, 44, 154, 155
Spawn, frog and toad, 766
Specific heats and quantum theory, 17, 217
Spectra, absorption, 152-163, 213, 214, 216, 218, 270, 271, 336, 337
of sterols during irradiation, 794-801
atomic, 19-22, 230
band, 19, 163, 216-228
continuous, 18, 19, 94, 152, 153, 229-236
convergence, 230, 246, 293-295
electron-affinity, 337, 338
for absorption studies, 152
line, 5, 18-23, 26
molecular, 19, 217-228, 230, 231, 234-236
of ions, 33
of polyatomic molecules, 223, 224
predissociation, 241-244
Raman, 222, 224
rotation-vibration, 221-223, 225
series, 23, 24
spark, 32, 33, 36, 42
Spectrograph, 183, 190, 270, 271
Spectrographic analysis, 662
Spectrometer, quartz, 693, 694
Spectrophotometers, photoelectric, 271
Spectroradiometer, 100
Spectroscopy, and photochemistry, 229-244, 270
Spectrum, electromagnetic, nature, 2, 3, 6, 7, 9, 10
of sunlamp, 144-146
solar, 4, 7, 174, 192
Spekker photometer, 161, 270
Sperm, 717, 764
Sperry arc, 618
Spin, of electrons, 25, 226
nuclear, 226
Spinach, irradiated, 742, 789, 830, 856
Spinal fluid, gold test, 677
Spindle oil, 653
Spirit black, 643
Spirocyclopentane, 810
Spirogyra, 685, 882
Spirostomum ambiguum, microirradiation, 703
Spleen, and typhoid immunization, 757
Splenic hormone, 749, 750, 757
Spores, 706, 711, 727
Springfield Lake, solar energy at, 198-200
Spruce 618, 876
Spyrogyra, ultramicroscopic irradiation, 717
Squalene, 511
Square root law, for rates, 251, 252, 254, 278
Stabilizers, 462, 657
Stability of colloidal systems, 387, 388
Stains, from methylene blue, 630, 631
Standards, of radiation, 99, 100
Stannates, and cotton, 615
Stannic acids, 366, 591
Stannic chloride, 489, 648
hydroxide sol, 390, 391
iodide, 240, 365, 366
oxide, 259
Stannous chloride, 365, 384
oxide, 171
Staphylococci, 706, 720, 727, 728, 825
Staphylococcus aureus, 694, 696, 697, 704, 705
phage, 712
Star spectra, 32-34
Starch, 267, 384, 435, 620, 681, 682, 791
photolysis, 435, 436
photosynthesis, 866-868, 882
Starfish eggs, 764
Stark effect, 163, 336
Stearates, 586
Stearic acid, 265, 266, 437, 554, 560, 574, 743
anilide, 265, 677
Stearoleic acid, 565
Steels, 661
Steenbock diet, 786
unit, 835, 838, 841
Stefan-Boltzmann law, 15-17
Stellar energy, origin, 191, 192
Stenobothrus spermatocytes, 704
Stereoisomerizations, 406, 412, 452-456, 482-484, 488, 490, 491, 564-567, 569, 596, 793
Stereoisomers, absorption by *cis* and *trans* forms, 453
"Sterilamps," 724
Sterilization, of food products, 721-724
of medicinal products, 725-728
of water, 125, 718-721
Sterols, 789, 791-801, 809, 827, 833, 834, 888
Stibine, 332
Stigmasterol, 7-dehydro, 817
Stilbazoles, polymerization, 521
Stilbene, 267, 490, 511, 548, 549, 648, 743
Stimulation of bacterial growth, 697
of cells by ultraviolet rays, 697, 704, 707
of paramecia, 717
of plant growth, 150, 887
of yeast growth, 708, 710
Stinging nettles, 657
Stokes's law, 207
Stratification, of suspensions, 391
Stratosphere, 193, 194
Stratum granulosum, 736
Straw pulp, 618
Streaming reactions, temperature coefficients, 248
Streptococci, 706, 727
Striated discharge, mercury vapor, 83
Strontium, 26, 57, 184
Strophanthus, tincture, 658
Strychnine, 525
Styrene, 173, 488, 489, 595
Styrolene, 548
1-Styryl-3-bromostyryl-4,6-dinitrobenzene, 471
4-Styryl-2,4-dichloro-3-cyanopyridine, 521
Substance 248 in ergosterol irradiation, 808, 811, 821
Substance L in ergosterol irradiation, 805, 807
Substance S in ergosterol irradiation, 800, 801
Succinic acid, 437, 438, 441, 447, 452, 454, 764
Succino-dehydrogenase, 686, 687
Sucrase, 682, 683
Sucrose, 260, 356, 371, 387, 433-435, 472, 521, 868, 890
Sugars, 500, 681, 682, 722
occurrence, 742, 858, 891
oxidation, 673
photosynthesis, 866, 870, 889 (see also Carbohydrate photosynthesis)
Sulfanilic acid, 500, 643
Sulfate ion, 355, 377
Sulfhydryl compounds, 463, 623, 676, 678, 679
Sulfides, 142, 583, 615
Sulfite cellulose, fluorescence, 620
Sulfites, 355, 356

Sulfobenzeneazo-*N*-phenyl-β-naphthylamine, 626
Sulfofluorene, 503
Sulfones, 489
Sulfonic acids, 519
Sulfophenyl-3-methyl-5-pyrazolone, 382
Sulfur, 141, 359, 390, 534, 600, 605, 607, 611, 620
and gasoline, 654
and oils, 558, 574
bacteria, 518
compounds, 379, 463, 464, 534, 653-655
fluorescence, 600, 601, 620
formation, 354, 358, 385, 463, 498
in vulcanization, 597-599
neutral, excretion, 745
occurrence, 608, 622, 623, 679, 756
oxidation, 354
pigment, 582
predissociation, 241, 244
reaction with arsenic, 354
reaction with hydrogen, 329
sensitizer, 479
sols, 387, 390
vapor, absorption spectrum, 329
Sulfur chlorides, 354, 355, 534, 545, 596, 599
dioxide, 69, 330, 332, 390, 407, 534, 590, 634, 654, 750
absorption spectrum, 330, 355
from wool, 622
in accelerated paint tests, 580
predissociation, 241, 243, 244, 330
monoxide, 330
oxygen acids, formation, 354
trioxide, 330
Sulfuric acid, 187, 339, 343, 354, 469, 484
effect on various photoreactions, 340, 358, 455, 524
formation, 331, 357, 457
Sulfurous acid, 354
Sulfuryl bromide, 332
Sulfuryl chloride, 331, 534, 545
Sulzin, 598
Sun, as ultraviolet source, 99, 191-202
"Sun Ray," 173
Sunburn, 673, 733
creams, 743
Sunflower, 886, 888
oil, 571, 574, 790
Sunlamp, 111, 141, 143-147, 561, 738, 783, 887
Alpine, 129, 134, 135
Sunlight, actinometry of, 35, 103-105
and rickets, 170, 778, 779, 781, 782, 787, 809, 828, 832, 837
antagonistic action of rays in, 150
energy distribution, 192, 195-202
tests of light-fastness of dyes, 634-636, 640-642
therapeutic use, 734, 769, 770, 772, 773
"Sunlit," 175
Sunspots, 2, 192
Suprasterols, 805, 808-811
Surface catalysts, 253, 254
designs, on rubber, 599
photoreactions in, 265
vulcanization, 598, 599
Swan bands, in carbon arc, 53
Swatch boxes, 640
Swimming pools, 147, 720
Swine, light sensitization, 861
"Sylphrap R R Old Gold," 561
Sympathetic system, 734, 760
Sympathicotonic action, 751
Symplex, of vitamin D and lactalbumin, 839
Synephrine, 689
Synergy, of radiations, 442, 443, 486, 873
Synthetic rubber, 409, 593

Tachysterol 807-811, 816, 821
Tadpoles, 759, 766
Taka-diastase, 681, 682
Tannic acid, 621
Tannin, 390
Tanning materials, 651
of skin, 671, 738, 739, 772
Tantalum, 58, 74, 97, 98
Tapes, insulating, 606
Tar cancers, 766
coal, 865
papillomas, 766
road, testing, 661
Tariric acid, 554
Tartar emetic, 359
Tartaric acid, 384, 407, 448, 450, 541, 648, 660, 672, 870, 883
oxidation, 364, 366, 448, 450
Tartrates, 353, 377
Tea, 660
Teaseed oil, 555
Teeth, 178, 824
Television, 150
Telfairia oil, 574
Tellurium, 148, 384
oxide, 354
Temperature, after body irradiation, 744
and absorption spectra of solutions, 337
and black body radiation, 15-17
and photosynthesis in plants, 873, 874, 876, 882
effect on lamps, 132, 133, 139
coefficient, 245, 248-250, 252, 293, 443, 692, 693, 698, 708, 711, 716, 740
Tenderizing beef, 724
Tent fabrics, 615
Terephthaldehyde, 476, 481, 482
Terephthaldehydic acid, 476, 481
Terephthalic acid, 481
Terephthalophenone, 476
Terms, spectral, 23, 24, 234, 235
Terpenes, 514, 550, 659
Terpinol hydrate, 514
Tesla coil, 153
spark, 155
Test, accelerated weathering, asphalts, 661
dyes, 634-642
enamels and lacquers, 586, 587, 590
lithopone, 386
paints, 575-581
papers, 618
road tar, 661
rubber, 605-609
steels, 661
varnishes, 586, 587
Tetanus bacillus, 710
toxin, 690
Tetany, 755, 823, 826
Tetrabenzoylethylene, 489, 490, 493
Tetraborate ion, 377
Tetrabromofluorescein, sensitizer for Eder reaction, 444
Tetracarboxypyridine, 519
Tetrachloroanthraquinone, 550
Tetrachloroarsine, 549
Tetrachlorobenzene, 547
Tetrachlorodimethylbenzophenone, 478
Tetrachlorodimethylbenzoyl chloride, 548
Tetrachlorodithiacyclobutane, 464
Tetrachloroethane, 401, 526, 537, 613
Tetrachloroethylene, 534, 535, 657, 659
Tetrachloroketonaphthalene, 493
Tetrachloromethylpropane, 532
Tetrachloroplatinic acid, 248, 369, 370
Tetraconite, 613
Tetrafluorenylhydrazine, 511
Tetrahydrodiphenylnaphthacene, 510
Tetrahydronaphthalene, 613
Tetraleneacetic acid, 511
Tetralin, 501, 657
Tetramethoxyaminophenylcinnamic acid, 484
Tetramethoxyphenylcarbostyril, 484
Tetramethylene, nitrosochloride, 461
Tetramethylthiuramdisulfide, 598, 605, 612
Tetranitrodiammine cobalt, 368
Tetranitromethane, 36
Tetraoxybutyloxyquinoxaline, 851
Tetraoxybutylquinoxaline, 851
Tetraphenyldibenzoyltetrahydropyran, 521
Tetraphenyldihydropyridine, 521
Tetraphenyldihydrotriazine, 493
Tetraphenyldihydroxyethanedicarboxylic acid, lactone, 478
Tetraphenylrubene, 509
Tetraphenylrubrene, 510

Textile printing, 520, 645-647
Textiles, 499, 624, 641, 831
Thallium, 150, 238, 257, 369, 377, 380, 744
  bromide, 238
  chloride, 183, 238, 350
  iodide, 238, 345
Theosterols, 817
Therapy, 143, 150, 770-772, 862
  lamp, 132-134, 138, 139
Thermionic valve, 97
Thermochemistry, 217
Thermocouple, 771
Thermodynamics, and photochemistry, 206, 212, 213
Thermoluminescence, of solarized glasses, 176
Thermophilic bacteria, 722
Thermopiles, 96, 99, 271, 697, 782
Thermostat, for carbon arc, 60
Thiamine, 850, 851
Thiazine dyes, 640, 712
Thiazole, amino, 498
Thiazoline, 183
Thiocarbamide, 498
Thiocarbanilide, 573, 605
Thiochrome, 851
Thiocresol, 415
Thiocyanic acid, 358
Thiocyanacetoneoxime, 494
Thiocyanogen, 457
Thiocystis, 707
Thioglycollic acid, 463
Thiohydrazides, condensation products of, 500
Thionine, 631
Thiophene, 466, 863
Thiophosgene, 463, 464
Thiopyronine, 712
Thiosemicarbazones, 495
Thiosinamine, 263, 264, 864
Thioxanthone dyes, 712
"Thiozone," 597
Thistle blossom rennet, 684
Thoracoplasties, 729
Thorium, 97, 98, 362
  dioxide, 870
  hydroxide sol, 390, 391
Thormaehlen reaction, 740
Threads, sterilization, 727
Thresholds, for lethal action, 699-701, 716
  for vitamin D_2 formation, 812
  photochemical, 246, 247, 290, 291, 327, 397, 480, 866
  photosynthesis of carbohydrates, 866
Thrombin, 684
Thrombocytes, 749, 825
Thrombocytogenesis, 749
Thrombopenia, 749
Thunberg tube, 686
Thyme oil, 513
Thymine, 518, 696, 699, 701, 702
  glycol, 518
Thymol, 513
Thymonucleic acid, 677, 698-701, 704
Thyroid gland, 689, 749, 759, 777
"Timonox," 582
Tin, 149, 150, 155, 171, 365, 366, 386, 657
  halides, 359, 411
Tinctures, deterioration, 658
Tires, fluorescence analysis, 600
Tissue cultures, 764, 765
  paper, 619, 620
  respiration, 863
Titanium, 26, 57-59, 78, 97-99, 172, 592, 743
  chlorides, 359, 369
  dioxide, 165-169, 458, 609, 612, 617, 673, 883
  nitride, 139
  oxide, 75, 152, 350, 386, 583, 598
  white, 575, 582, 590
"Titanox," 577, 582, 583
"Tithonometer," 284
Titrations, in Wood's light, 665
Tobacco, 522, 659, 660, 861
  cloth, 616
  disease virus, 712
  plants, 883, 884, 889
Töpler cloud, 285
Tolidine, 646, 721
Tolualdehydes, 469
Toluene, 467-469, 470, 480, 496, 506, 508, 514, 651
  acetyl, 547
  arsenic acid, 549
Tolueneazo-β-naphthol, 633, 634
  bromination, 545, 549
  chlorination, 526, 542, 544, 545
  chloro, 544, 549
  hexahydro, 424, 473
  nitro, 470-472
  sulfonanilide, 587
Toluhydroquinone, 474
Toluic aldehyde, 468
Toluidine Blue, 632
  Green, 632
Toluidines, 495, 497, 647
Toluquinone, 474
Tolylbenzoic acid, 478
1,1′-*bis*(*p*-Tolyl)-3,3′-diphenyl-5,5′-dimethylrubrene, 510
Tolylglyoxime, 461
Tolylquinoline, 521
Tomato bushy stunt virus, 712
  plants, 887-889
"Toplast," 589
Torch, oxyacetylene, 164
Tortelli-Jaffe reaction, 796
Tortoise shell, bleaching, 649
Torula, 685
Toxascaris Leonina, ova, 718
Toxic calcification factor, 821
Toxicity, mercury, 124
  vitamin D, 820-823
Toxins, 690, 691, 860
Toxisterol, 808, 811, 821
Toxocara ova, 718
Tracing cloth, 189
Transformer oils, 651
Transformers, 40, 42, 135, 136, 139, 140, 144, 147, 153-155, 159, 162
Transitions, between energy states, 219-223, 225
  forbidden, 24, 92
Transpiration, 867, 874
Trehalose, hydrolysis, 434
Triacetin, 650
Triacetoxytriethanolamine, in stabilizing gasolines, 655
Triaminotriphenylmethane, 626
Triarylacetonitriles, 627
Triazine tetraphenyldihydro, 493
Triazolium salts, 626
Tribromoethyl alcohol, 658
Tribulus terrestris, as photosensitizer, 861
Tributyl phthalate, 576
Trichloracetic acid, 249, 452
Trichloroacetyl chloride, 534, 535
Trichloroacetyltrichloromethylbenzene, 547
Trichlorobenzene, 543, 547
Trichlorobromomethane, 211, 215
Trichlorocineole, 550
Trichloro-2,4-dimethylbenzoyl chloride, 548
Trichloroethane, 534
Trichloroethylene, 401, 407, 529, 535, 657
Trichlorohydrin, 534
Trichloroiodobenzene, 544
Trichloroisobutane, 532
Trichloromethylpropane, 532
Trichloropropane, 534
Tricresyl phosphate, 576, 590, 591
Triethanolamine, 833
Trifolium, 715
Trihexosan, 435
Trihydroxyanthraquinone Purpurin, 616
Trihydroxytriethylamine derivatives, 183
Tri-iodide ion, 249, 446
Trimethylacetaldehyde, 421
Trimethylamine, and visual purple, 858
Trimethylenechlorobromide, 550
Trimethylethylene, 394, 594
Trimethyliodostannane, 366
Trimethylisoalloxazine, 852
Trimethylmethane derivatives, 267
Trimethylpentane, 464

Trinitrobenzaldehyde, 475
Trinitrobenzene, and rubber vulcanization, 598
Trinitrobenzoic acids, 472
Trinitrobenzoyl alcohol, 472
Trinitrobenzyl bromide, 472
Trinitrostilbene, 266, 267
Trinitrotoluene, 354, 471, 472
Trinitrotriammine cobalt, 368
Triolein, 558
Triose, 435, 436
Triphenylbromomethane, 626
Triphenylchloromethane, 626, 627
Triphenylfulgide, 493
Triphenylguanidine, 605, 610
Triphenylhydroxypropionic acid, 477, 478
Triphenyllactic acid, 477, 478
Triphenylmethane and derivatives, 267, 626-629, 632, 640
Triphenylnaphthacene, 511
Triphenyl peroxide, 626
Triphenyl phosphate, 173, 590
Triphenylrubrene, 510, 511
Trisilane, 333
Trisodium phosphate, 440
Trisulfon Violet, 639
Tritolyl phosphate, 587, 589, 591
Triton embryos, 765
Tropacocaine, 436
Tropaeolum majus, photosynthesis, 868
"Tru-hu" silk crêpe, 642
Truxilldiamide, 484
Truxillic acid, 483, 484, 491
Truxinic acid, 483, 491
Truxinic anhydride, 484
Truxones, 492, 493, 517
Trypaflavine, 261, 264, 861, 862
Trypan Blue, 634
  Red, 634
Trypsin, 680, 684
Tryptophane, 670-674, 682, 683, 696, 701, 737, 739, 748, 764, 863
Tsubaki oil, oxidation, 559
Tubercle bacilli, 699, 706, 775
Tuberculin, 690
Tuberculinic acid, 700
Tuberculosis, 733, 771-773, 823
Tumors, 150, 742, 766, 865
Tuna fish liver oil, 801, 815-817
Tung oil, 386, 559, 564-567, 571, 648
Tungstates, and cotton, 615
Tungsten, 58, 59, 74, 75, 78-80, 143, 145, 149, 156, 161, 369
  lamp, 34, 35, 156, 160, 693, 694
  spark, 152, 154, 155
Tungsten carbide, 51
  trioxide, 369
Tungstic acid, 369, 387, 418, 433
Turkey-red oil, 382, 613
Turnip seeds, 716, 885
Turpentine, 513, 514, 610
Tyndall cone, 387
Typhoid bacillus, 720, 757, 775, 825
Tyrosinase, 684
Tyrosine, 670-674, 682, 684, 696, 701, 737, 739, 741, 791, 863

Ubands, in halide crystals, 375
Ulcers, 862
Ultrament, 562
Ultramicroscopic irradiation of protozoa, 717
Ultramicroscopy, of dried oils, 567
"Ultratuberculin," 690
"Ultraviol," 175
Ultraviolet microscopy, 703, 704, 715
Ultraviolet-permeable glasses, 168-176
Ultraviolet plates, 381, 382
  radiations, 2, 6, 7, 164, 208, 498
Ultraviolet-sensitive papers, 383
Ultraviolet-transmitting materials, 172-176
"Ultrazin," 166
Ulva lactuca, photosynthesis by, 874
Umbelliferoneacetic acid, 562
Undecenic acid, 553
Units, for milk irradiation, 842, 843, 845, 846
Units, photosynthetic, 881
  vitamin D, 781, 819, 820
  wave-length, 5
Unsaturated acids, bromination, 554
  compounds, aliphatic, 406-415
  hydrocarbons, halogenation, 533-538
  oils, detection, 558
Uracil, 677, 683, 696, 699, 701-703, 850
Uranic salts, 361
Uranin, 261
Uranium, 58, 97-99, 103-105, 155, 169, 370
  acetate, 834
  ferrocyanide sol, 391
  nitrate, 178
  oxides, 166, 630, 868
  salts, 359, 362, 370, 403, 407, 432, 450, 468, 727
Uranous sulfate, 370
Uranyl acetate, 448, 525
  chloride, 489
  nitrate, 405, 411, 442, 449, 481, 503, 812
  oxalate, 102, 104, 418, 443, 459
  salts, 259, 261, 336, 409, 439, 440, 443, 447, 451, 452
  sulfate, 104, 307, 447
Urea, 171, 173, 356, 436, 498, 688, 760
  condensation with formaldehyde, 172, 584
  derivative of aminobenzoylphenylenediamine, 562
  diethyldiphenyl, 354
  formation, 350, 518, 702
  of 4-aminobenzoyl-3-aminopyrenedisulfonate, 562, 563
  photolysis, 458, 459
Urease, 683, 684
Urethane, and quinine, 523
Uric acid, 187, 350, 702, 703, 863
Urine volume, 745
Urobilin, 750
Urobilinogen, 871
Uroflavin, 851
Uronic acid, 883
"Uroxameter," 103
"Ursilber," 379
Urticaria, 824, 861, 862
Uterus, 760
"Uviarc," 80, 81, 85-87, 89, 92, 100, 117, 129, 134-137, 174, 175
"Uviol," 156, 173, 175, 176, 178, 182, 305
  lamps, 108, 114, 182
"UVscope," 100

Vaccination, 713, 775
Vaccines, bacterial, 725, 726
Vaccinia virus, 712, 725
Vagotonic action, 751
Vagus, 734, 746
Valine, 671
Valve, thermionic, 97
Vanadium, 26, 58, 169
  oxide, 75, 152, 165-167, 508
  salts, 409, 592
Vanillin, 498, 514, 558
Van Slyke test for amino groups, 622
Varnishes, 407, 566, 573, 586, 587, 648
Vaseline, 381, 462, 600, 610, 727
Vasoconstriction, 747
Vasodilatation, 747
Vat dyes, 616, 617, 630, 642, 647
Vegetable extracts, 722
  oils, 557, 789
Vegetables, vitamin D in, 827
Venom, cobra, 691
Vermillion, 386
Veterinary medicine, irradiation therapy in, 777, 785, 786
"Viat," 173
Vibrational energy, 218, 220, 222, 223, 227, 229, 230, 233-236, 247, 250
Vibrationless state, 233
Vicia faba, leaves, 715
Victor water-cooled mercury arc, 701
Victoria dyes, 636, 639, 554
Vigantol, 759, 820, 821, 825, 832, 833
Villikinin, 689
Vinyl acetate, 172, 173, 410, 411, 585
  anisole, 410

Vinyl bromide, 409, 410
chloride, 409-411, 534, 585
chloroacetate, 173
diazomethane, 460
esters, polymerization, 173, 410, 411
ethinylcarbinols, 410, 411
halides, 205, 410, 411
iodide, 399
resin, 410-412, 619
Violet N, 639
Violin strings, sterilization, 727
"Viopake," 166
Viosterol, 742, 820, 823-827, 831
Vipera Russellii, toxin, 691
Viruses, 711-713, 860
Viscose, 188, 585, 613, 615, 616, 619-621
Viscosity, and fluorescence quenching, 335
Visibility, sensitivity curve, 180
short wave-length limit, 762
Visible rays, 2-4, 6, 178, 208, 680, 692
Vision, 856-859
Visual yellow, 858
purple, 857-859
"Vitaglass," 103, 104, 169, 172-175, 178, 181, 637, 661, 711, 712, 776, 782, 825, 887, 888
Vital staining, 751
"Vitamalt," 832
Vitamin, antihemorrhagic, 856
fat-soluble, 780
preparations, standardization, 834
production, 848
Vitamin A, 814, 825, 828, 846, 848, 857, 858
absorption spectrum, 853
assay, 780, 853, 854, 856
in cod-liver oil, 831
not produced by irradiation, 780, 790
photolysis, 854-856
Vitamin A_2, 853
Vitamin B group, 688, 850-853
Vitamin C, 660, 740, 743, 755, 785, 846, 848, 849
Vitamin D, absorption spectrum, 796-799, 804
and infections, 823-825
and public health, 831
assay, 780, 785, 805
crystalline, 800, 801, 803-807
destruction, 721, 793, 797, 801, 803, 805
dosage, 802, 803, 819, 820
emulsion, 834
for animals, 786, 788, 838
formation, 103, 150, 733, 803, 804, 814, 832
in human milk, 785
in wine, 660
local application, 847
natural, 813, 814, 816
origin in fish-livers, 790
physiological action, 780, 785, 818, 819, 824, 827
response of rats and chicks, 814, 817
toxicity, 785, 820-823
unit, 781, 819, 820, 835
Vitamin D_1, 806, 807, 821
Vitamin D_2, 803, 807, 808-811, 813-817, 821, 822, 834
Vitamin D_3, 816, 817, 821, 831
Vitamin D_4, 813
Vitamin E, 856
Vitreous humor, transparency, 762, 764
"Vitrisol," 742
Voandzeia, 715
Voltaic cells, irradiation of, 105
Vorticella, 523
Vulcanization, 596-599, 601, 604, 605
Vulcanized rubber, 593, 597, 601, 606-608, 609
Vulkan colors, 599
Vuzin, 524

Warburg respiratory enzyme, 687
Washington, solar energy at, 195, 198
Water, 359
absorption, 183, 194, 298, 299, 338
bands, fluorescence, 304
dissociation, 231, 240, 299, 302
effect of x-rays on, 209
effect on carbon dioxide photolysis, 307, 308
effect on hydrogen-chlorine combination, 286-288
Water, filters, 183
formation, 299, 302-304, 422
irradiated, 710, 720
photolysis, 299, 339
reaction with bromine, 345
sterilization, 718-721
Water gas, 259, 481
Water-glass, 385
Waterproofing paper, 620
Wave-length, and temperature coefficients, 249, 250
characterizing radiations, 10, 11
conversion to wave-number, 208
optimum for lethal action, 698, 701
effective for milk irradiation, 843, 844
effective in rickets, 780, 781, 809
effective in therapy, 773
erythema-producing, 737, 738
for lethal action on yeast, 708
kcal, equivalent of, 207, 208
measurement, 4, 5
restricted, in irradiation of ergosterol, 833, 834
synergy of, 450
Wave mechanics (see Quantum mechanics)
Wave-number, 5, 208, 222, 224
Wave theory, 3, 4, 6, 10
Waves, 2, 3, 4, 6
Wax, carnauba, 608
ceresin, 610
Japan, 586
Montan, in rubber, 610
white, 534
Waxes, fluorescence, 600
Weather-Ometer, 587
Wedges, platinum for reducing light intensity, 270
Wehnelt cathodes, 76, 156
Weigert effect, 266, 383
Welding, injury to eyes, 164
Weston photronic cell, 97
Whale oil, 555, 557
Wheat, 829, 830, 883
Whitby test for cholesterol, 793
White cells (see Leucocytes)
White lead, 582, 583
Whiting, in rubber, 610
Whiskey, aging, 660
Whooping cough, 775
Wien's displacement law, 15, 16, 94, 155
Willemite, 190
Window glass, 170, 174, 175
Wine, aging, 660
Wintergreen oil, 513
Winter sunlight, and rickets, 781, 782
Witte's peptone, 674, 688, 691
Wood, 611, 612, 617-619, 648
Wood's light, 461, 752, 781, 849
Wool, 188, 189, 613, 616, 618, 622, 623, 678, 679
and dyes, 471, 635, 637, 639, 501, 502
chlorination, 550
fat, irradiated, 847
fluorescence, 624, 645
Green, 642
mold growth on, 727
Woolen patterns, 642, 643
Wormseed oil, 513
Worsteds, 636, 640, 642
Wort, irradiation, 710
Wound healing, 729, 770
Wrappers, protective, 560-563
Würtzite, 385

Xanthene dyes, 640
Xanthine, 702
Xanthine oxidase, 686
Xanthogenation, 617
Xanthone, 507
Xanthophyll, 856, 858, 871, 872, 876, 882, 888
Xanthorhamnin, 436
Xanthydrol, 592
Xenon lamp, 151, 300, 308, 319, 393
Xeroderma pigmentosum, 769, 861
Xerophthalmia, 780
X-rays, 2, 7-9, 354, 657
and foodstuffs, 828
and proteins, 677
and sterols, 803, 804, 832

X-rays, biological actions of, 705, 708, 733
reactions by, 208, 209
Xylene, 467-469, 503, 545, 546, 651, 829
Xylidine, 497, 647
Xylyl chloride, 546

Yarns, 613, 615
Yeast, absorption spectrum, 708
and glucolysis, 710
antirachitic activation of, 837
autolyzates, 682, 683, 837, 847
catalase content, 685
destruction of B vitamins in, 850
effects of irradiation of, 707-710, 727, 789
ergosterol content, 795
extract, 686, 837
growth, 563, 708, 709
gums, 682
proteinase, 683
respiration, 687, 688, 709, 750
susceptibility to lethal action of rays, 696, 706
Yellow oxidation enzyme, 853
Yttrium compounds, 58, 142

Zapon lacquer, sensitizer, 479
Zea mais, seedlings, 888
Zeeman effect, 24
Zero branch, 223
Zero-point energy, 227, 233, 235, 290
Ziehl-Neelsen stain, 706
Zinc, 97, 147, 150, 151, 169, 171, 190, 385, 541
and fatty acids, 554
arc, 62, 64, 231
corrosion, 661
glass, 165
heat of dissociation, 234
in carbon arc, 57
in tissues, 760
lamp, 148-150
Zinc, plates, and aniline, 495
soaps, 586
sols, 387, 388
spark, 154, 155
wool, 401
Zinc blende, 385
carbonate, 869
chloride, 64, 171, 519, 532
chromate, 583
diethyl, 464
diethyldithiocarbamate, 605
dimethyl, 464
disulfide, 385
halides, 240, 411
nitride, 64
oxide, 169, 171, 178, 575, 590, 605, 831
and dyes, 630
and nitrate reduction, 354
as photosensitizer, 259, 339, 350, 370, 371, 458, 500, 553, 625, 673, 883
fluorescence analysis, 600, 601
in carbohydrate photosynthesis, 869
in nitrocellulose lacquers, 580, 589
in rubber, 598, 599, 603, 607, 610, 611
opacity, 582
paints, 577, 580
reflecting power, 583
oxynitrate, 371
peroxide, 573
resinates, 585
salicylate, 621
silicate, 142
sulfide, 384, 385, 590, 600, 743
actinometer, 104, 105, 202, 717
xanthate, 596
Zirconium, 58, 59, 362
nitride, 139
oxide, 141
Zones, in crystals, 374, 375
Zoöplankton, 790
Zwitterions, 671
Zygote, 717
Zymosterol, 795

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